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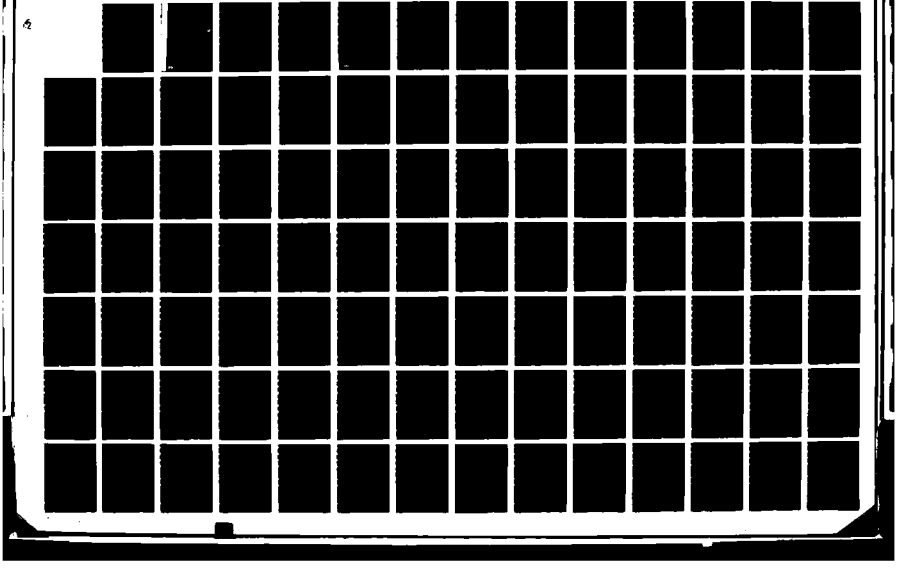

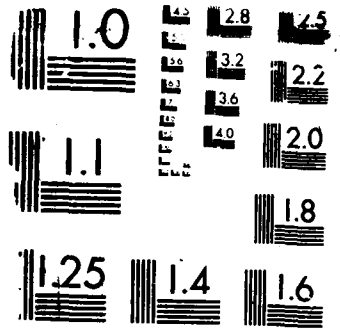

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AFOSR-TR- 87-1690

ORDERED POLYMERS FOR SPACE APPLICATIONS

October 1987

Final Scientific Report

By: James F. Wolfe, Steven P. Bitler, and Andrea W. Chow

Prepared for:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Directorate of Chemical and Atmospheric Sciences
Building 410
Bolling Air Force Base
Washington, DC 20332-6448

Attention: Major Larry P. Davis

Contract No. F49620-85-K-0015

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SRI International
333 Ravenswood Avenue
Menlo Park, California 94025-3493
(415) 326-6200
TWX: 910-373-2046
Telex: 334486

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The synthesis of polybenzazole (PBZ) polymers and model compounds was studied to determine their (1) potential for use in nonlinear optical (NLO) applications and (2) reaction kinetics and chemo-rheology of polymerization in the ordered phase. Specific compounds that should exhibit high figures of merit in NLO applications have been identified. The synthesis of PBZ polymers with controlled molecular weight is described, including a description of the synthesis variables important in attaining high intrinsic viscosity and low shear viscosity nematic solutions, leading to improved processability and reproducibility. The phenomenon of mesophase-enhanced polymerization of poly(p-phenylenebenzobisthiazole) (PBT) and the chemo-rheological properties at various shear rates were investigated. (polymers) ←

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Approved by:

D. D. Macdonald, Laboratory Director
Chemistry Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

SRI International®

333 Ravenswood Ave. • Menlo Park, CA 94025
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BACKGROUND

Ten years ago the Air Force Materials Laboratory and the Air Force Office of Scientific Research identified an area of research called the Ordered Polymers Program aimed at the synthesis and processing of particularly rigid polymers for use in aerospace vehicles where the properties of high strength, high modulus, and environmental stability were the key goals. Guided by earlier work on the rigid polymer BBL, initial research focused on "rigid rod" aromatic heterocyclic structures, namely poly(p-phenylene-2,6-benzobisthiazole) (PBT) and poly(p-phenylene-2,6-benzobisoxazole) (PBO). The structure-property relationships that originally led to the molecular design of PBT and PBO were (1) the rigid rod structure to impart liquid crystalline orderability and (2) a wholly aromatic structure to impart high modulus and thermal and thermooxidative stability. The fully conjugated nature of these π-electron systems now makes them good candidates for nonlinear optical (NLO) applications.

The use of organic polymers for NLO processes is gaining increased attention because of the ability to engineer molecular structures that have high laser damage thresholds, high values of both the first and second hyperpolarizabilities, and inherently fast response times. This general class of materials also provides synthesis and processing options that are not feasible with inorganic crystals, such as structural optimization through modification, fiber spinning, film casting, and thermoplastic processes.

This report provides the synthesis method for a class of polymers commonly referred to as PBZ polymers. One of these polymers, namely PBT has been shown to have a high value of the macroscopic third order optical nonlinear susceptibility, $\chi^{(3)}$. Development of the synthesis of these π-electron conjugated systems combined with their evaluation for NLO responses may be viewed to be the preliminary step in the engineering of optimized materials for use in optical signal processing devices of the future. By describing the process of preparing rigid rod and semi-rigid benzothiazole and benzoxazole polymers in poly(phosphoric) acid (PPA) at the appropriate concentration to achieve the advantages of the ordered solution morphologies, we establish the foundation for the preparation of materials with optimized figures of merit for NLO applications.

SUMMARY

During the last year of this contract, we identified specific compounds that should exhibit high figures of merit in NLO applications and explored the synthesis of model compounds and oligomers of this family of materials. Our approach was to explore synthesis methods that offered the potential for ordering these NLO active units in various ways in addition to the traditional nematic high molecular weight polymer systems exemplified by liquid crystalline poly(p-phenylenebenzobisthiazole) (PBT).

The goals of the current research are to

- Identify and synthesize NLO materials.
- Determine the dilute solution properties of PBZs.
- Conduct rheological studies of concentrated PBZ/PPA reaction mixtures.

Organic compounds with high values of the first and second hyperpolarizabilities are sought for fast optical signal processing. Devices from these compounds cannot be fabricated until enough data on NLO properties and chemical characteristics are compiled. Successful device fabrication requires materials that have high macroscopic susceptabilities ($\chi^{(2)}$ and $\chi^{(3)}$) as well as (1) good environmental stability, (2) processibility and fabricability (e.g., ability to form optical quality thin films or crystals), (3) thermal stability (stability at 1 GW/cm^2), and (4) fast switching times (subpicosecond).

Poly(p-phenylenebenzobisthiazole) (PBT) prepared at SRI has been processed into optical quality thin films with good optical response ($\chi^{(3)}$ = 50-100 x 10^{-12} esu)[1,2]. The model compound 2,6-diphenylbenzo[1,2-d:4,5-d']bisthiazole (trans-BTZ) prepared at SRI was measured by Garito et al. at $\chi^{(3)}$ = 0.19 x 10^{-12} esu. These results indicate NLO activity for the PBZ family of materials; therefore, the next step is to use the NLO active unit in polymeric systems that can more readily be processed into device shapes. Our goal is to prepare materials incorporating NLO active organic moieties formulated as main chain or side chain mesogens attached with flexible spacers or synthesized as a lyotropic polymer chain (polybenzazole type liquid crystalline polymer).

The synthesis of polybenzazole (PBZ) polymers having controlled molecular weights is described in our paper from the ACS Conference held in Denver, Colorado, in April 1987 entitled "Rigid Aromatic Heterocyclic Polymers: Synthesis of Polymers and Oligomers Containing Benzazole Units for Electrooptic Applications" (Appendix A). By controlling the molecular weight at relatively high levels, we aim to improve the processability and reproducibility of solutions for better optical quality high strength films. We have defined the variables of the PPA polymerization sufficiently to allow reproducible attainment of a specific intrinsic viscosity and other key dope characteristics including the shear viscosity of the dope and the morphology. The important synthesis variables to control are the DABDT purity, the concentration of the condensing species, the P_2O_5 content during polymerization, and the amount of endcapping agent used. We correlate

the experimental endcapping results with calculated values based on Flory's equations for condensation polymerization.[3]

We are submitting a paper to POLYMER entitled "Reaction Kinetics and Chemo-Rheology of Poly(p-phenylenebenzobisthiazole) Polymerization in the Ordered Phase" (Appendix B). The phenomenon of mesophase-enhanced polymerization of rodlike polymer PBT at 15% by weight in poly(phosphoric acid) was investigated. The reacting mixture became anisotropic at an early stage of the polymerization. The reaction rate increases significantly at the isotropic-nematic phase transition as the rods are aligned in positions more favorable for the condensation reaction to occur. The chemo-rheological properties at high shear rates ($\geq 10\ s^{-1}$), but not at low shear rates ($\leq 5\ s^{-1}$), also indicate the occurrence of the phase change. A systematic study on the effects of shear rate and temperature suggests that the initial mixing of the monomer mixture below the polymerization temperature greatly influences the final achievable molecular weight of the polycondensation reaction.

SYNTHESIS OF POTENTIALLY NLO ACTIVE ORGANIC COMPOUNDS

We have prepared a series of aromatic heterocyclic compounds that form the foundation of our approach to prepare nonlinear optical materials. These compounds have been designed with specific functionality to possess a high dipole moment and conjugated structures and to allow attachment to polymer systems.

The synthesis of model compounds under the current contract has resulted in the identification of routes to materials that are expected to be processible and possess NLO activity. One approach to processibility involves connecting various PBZ NLO active mesogens that we have prepared with flexible spacers to yield pendant or main chain mesogenic polymers. If readily processible, these polymers would have NLO units that are similar in length to the expected conjugation length of PBT polymers, thus achieving a polymer with regularly spaced NLO units.

Compounds analogous to those in this report can be synthesized that potentially would have a longer conjugation length. Work by Dalton et al.[4] has shown that the delocalization length in ladder polymers is about 26-28 carbon atoms. We can prepare NLO pendants of various lengths through the appropriate combination of monomer and capping group.

One route to a main chain mesogenic flexible polymer involves 2,6-di(4-hydroxyphenyl)benzo[1,2-d:4,5-d']bisthiazole (1). This compound should be incorporated into the backbone of a polymer chain by reaction with $ClCO(CH_2)_nCOCl$ to form a polyester as shown in Figure 1.

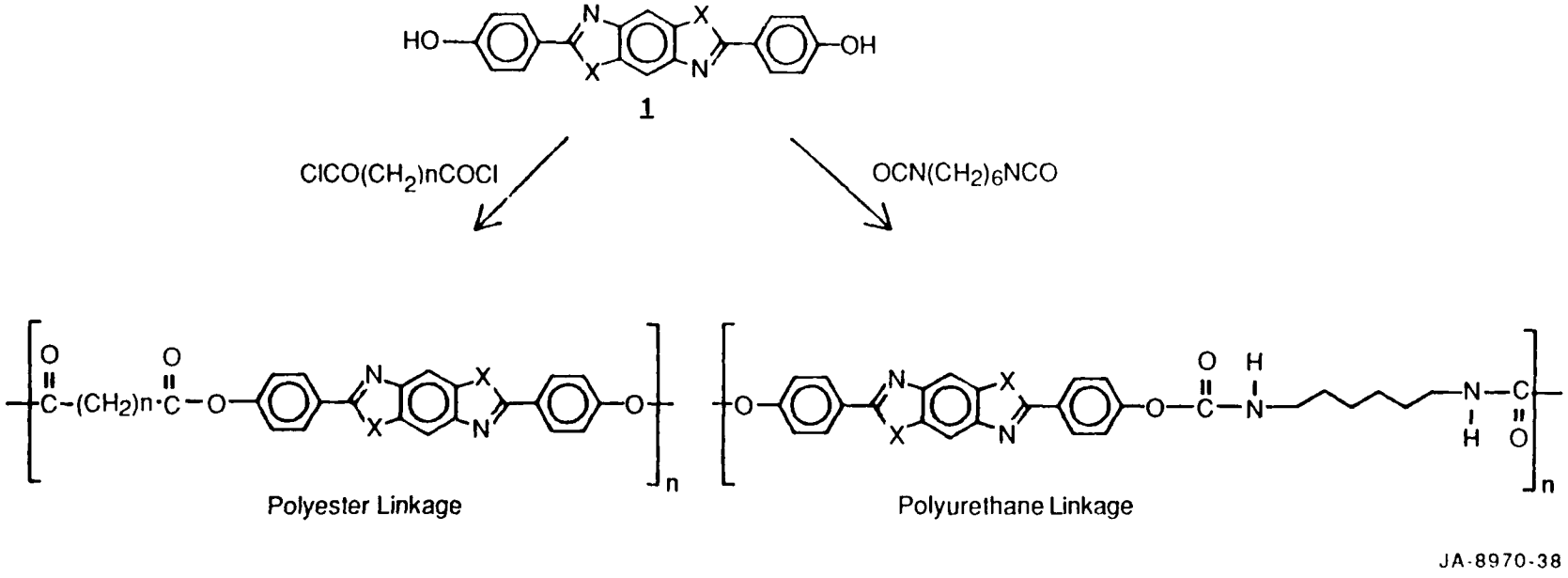


Figure 1 Preparation of flexible polymers with mesogenic compound 1.

The value of n can be varied to adjust the flexibility of the polymer and thereby the glass transition temperature, T_g, or the polymer melt temperature, T_m. The analog of 1 with $-NH_2$ groups at the terminal positions can similarly be prepared, yielding the polyamide after reaction with $ClCO(CH_2)_nCOCl$. Depending on the value of n, these polymers may act as liquid crystalline materials. A polyurethane polymer could also be prepared by reacting 1 with diisocyanates, such as 1,6-diisocyanatohexane or tolylene-2,4-diisocyanate.

Compound 1 has been synthesized by the reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) with 2 equivalents of 4-hydroxybenzoic acid in poly(phosphoric acid) (PPA). The polymerization reactions have not been conducted to date and will be pursued under our next contract.

Preparation of flexible polymers with pendant mesogens could use 2-(4-dialkylaminophenyl)-6-carboxybenzoxazole (2). This compound should be incorporated as a side chain liquid crystal on a flexible polymer backbone through the terminal carboxy group as shown in Figure 2. Forming the acid chloride of (2) should yield a more reactive starting material. The acid chloride of compound 2 can then be allowed to react with a triol or triamine. The resulting compound can then be polymerized by reacting this compound with a diacid chloride to form a polyester or polyamide or with a diisocyanate to form a polyurethane. The resulting polymer will contain liquid crystal side chains that are also NLO active.

Compound 2 has been prepared by reacting 4-dialkylaminobenzoic acid with 4-amino-3-hydroxybenzoic acid in PPA. The polymerization

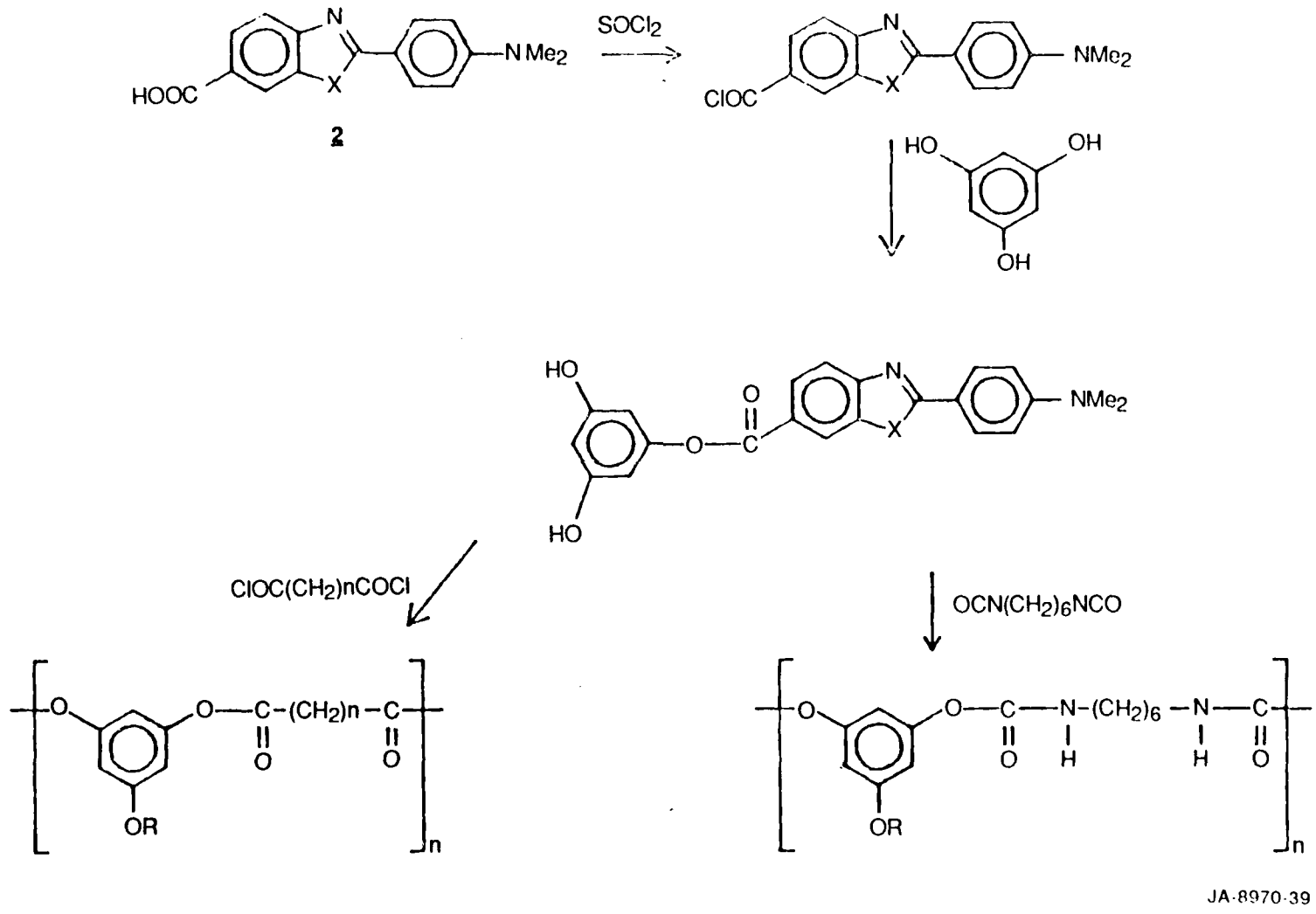


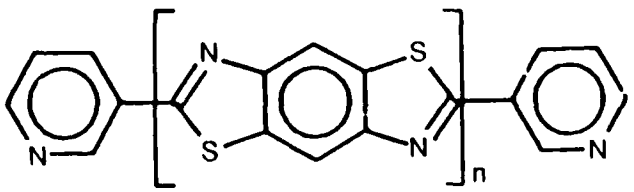
Figure 2 Preparation of flexible polymers with mesogenic compound 2.

reactions have not yet been conducted and will be pursued under our next contract.

Polymer attachment or functionalization is also possible with 2,6-di(3-pyridyl)benzo[1,2-d:4,5-d']bisthiazole (3), as shown in Figure 3, through attachment to the pyridyl nitrogens. Reaction with alkyl halides would form pyridinium halides. Compound 3 was prepared by reaction of DABDT with nicotinic acid in PPA.

We have also prepared model compounds and polymers with various endcapping agents to determine whether the presence of groups that affect the monomer electronics has an effect on the polymerization reaction. For example, 2,6-di(4-dimethylaminophenyl)benzo[1,2-d:4,5-d']bisthiazole (4) (Figure 3, n = 1) has been prepared. The analogous polymer 4, Figure 3, was prepared by reaction of DABDT and 99.5 mol% terephthalic acid. To the polymerization mixture was added 1 mol% 4-dimethylaminobenzoic acid. The resultant polymer was determined to have an intrinsic viscosity of 16.6 dL/g, a value similar to polymerizations using benzoic acid endcapper. The attempted preparation of model compounds in PPA with 4-nitrobenzoic acid yielded predominently black decomposed products, as discussed below; therefore, 4-nitrobenzoic acid was not used a capping group in polymerizations.

The presence of terminal nitro functionality results in products with potentially high dipole moments, particularly when combined with amino functionality at the other end of the unsaturated organic system. The most direct approach to preparing these compounds is to condense one molecule containing the nitro group with another molecule containing the amino group. This strategy was attempted in the preparation of 2-(4-dimethylaminophenyl)-6-nitrobenzoxazole (5),n = 0, Figure 3, and



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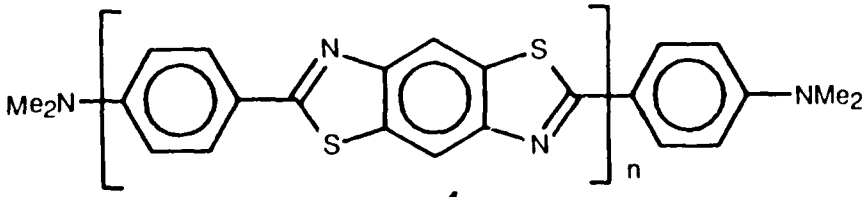

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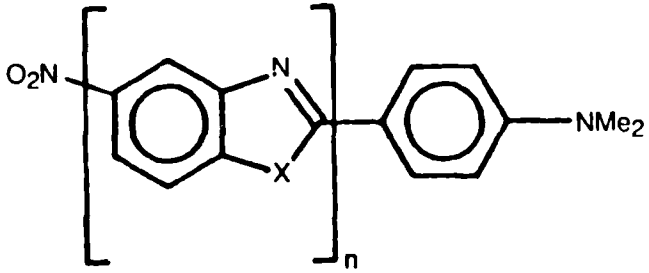
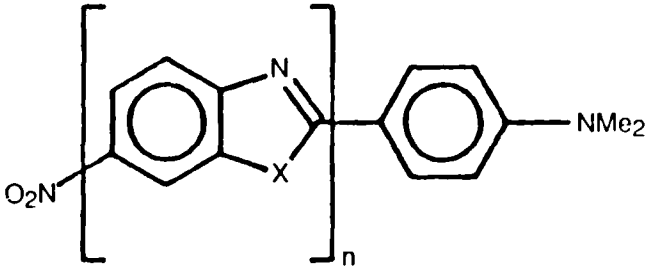


5 (X = O,S)



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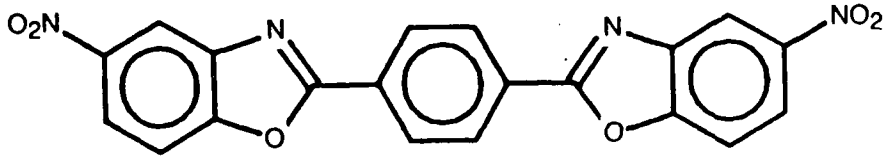

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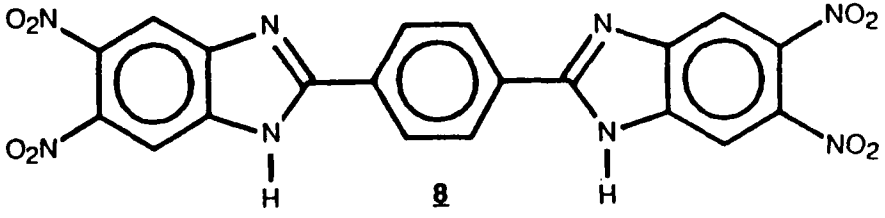

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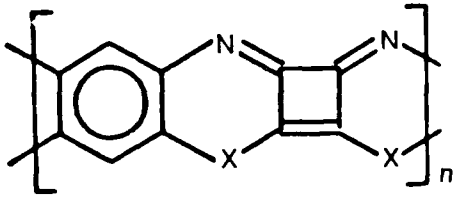

10 (X = S,O)

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Figure 3 NLO model compounds.

2-(4-dimethylaminophenyl)-5-nitrobenzoxazole (6),n = 0, Figure 3.

Condensation of 4-dimethylaminobenzoic acid and 4-nitro-2-aminophenol in PPA yielded a brown solid from which approximately 1% of the desired compound ,5, could be sublimed. Condensation of 4-dimethylaminobenzoic acid with 5-nitro-2-aminophenol in PPA to yield 6 produced only a brown solid from which no product could be sublimed. These results indicate that the predominant reaction pathway in PPA is decomposition resulting from oxidation of one reactant by the electron deficient nitro group.

To determine if similar compounds can indeed be prepared in relatively good yields, we heated a ground mixture of 4-nitro-2-aminophenol and terephthaloyl chloride to 225°C for 6 hours to produce 1,4-bis(5-nitrobenzoxazol-2-yl)benzene (7), Figure 3. We also heated a ground mixture of 4,5-dinitro-1,2-diaminobenzene and terephthaloyl chloride to 225°C for 6 hours to produce 1,4-bis(5,6-dinitrobenzimidazol-2-yl)benzene (8), Figure 3. The products were black solids that gave the correct mass spectral results, further suggesting that the nitro group causes decomposition in strong acid at high temperature.

The poor results for the condensation reaction of compounds containing nitro functionality in PPA suggest the alternative synthesis of these materials by a multistep process in which the benzazole unit is formed initially by condensation in PPA, followed by transformation of a functional precursor to the desired electron-donating or -withdrawing group. From our experience, using 4-dimethylaminobenzoic acid as an endcapper, electron-donating groups should be stable to the condensation conditions and will be present from the start. Electron-withdrawing

groups will be formed later by other methods, for example, the oxidation of an amino group to a nitro group.

A series of compounds with various conjugation lengths and dipole moments can be prepared by adding measured amounts of the AB monomers 3-amino-4-hydroxybenzoic acid and 4-amino-3-hydroxybenzoic acid to the reaction mixtures to produce compounds 5 and 6, respectively. Compound 6 should have a longer delocalization length with the electron-withdrawing group para to the nitrogen of the oxazole instead of meta as in 5.

These two compounds can be used to study the effects of delocalization on NLO properties. These compounds may be formulated as liquid crystalline polymers or oligomers that should have high microscopic susceptibilities because of the strong dipole moment caused by the electron-accepting nitro group opposite the electron donating amino group. By varying the amount of capping agent, we can prepare an oligomeric series that allows correlation of the NLO response with chain length. Preparing compounds 5 and 6 will be attempted in our next contract by condensing dialkylaminobenzoic acid with the appropriate amino substituted 2-aminophenol. The next step will be oxidation of the terminal amino group to a nitro group, as shown in Figure 4.

Our collaboration with Professor Anthony Garito of the University of Pennsylvania has resulted in the measurement of the nonlinear optical properties of 2,6-diphenylbenzo[1,2-d:4,5-d']bisthiazole (trans-BTZ), Figure 5. Professor Garito's research group has determined the third harmonic susceptibility $\chi^{(3)}$ of trans-BTZ to be 0.19×10^{-12} esu in the isotropic liquid state relative to glass at a wavelength of 1.907 um (0.65 eV) (see Appendix C). The frequency-dependent microscopic susceptibility was calculated by Professor Garito's group to be

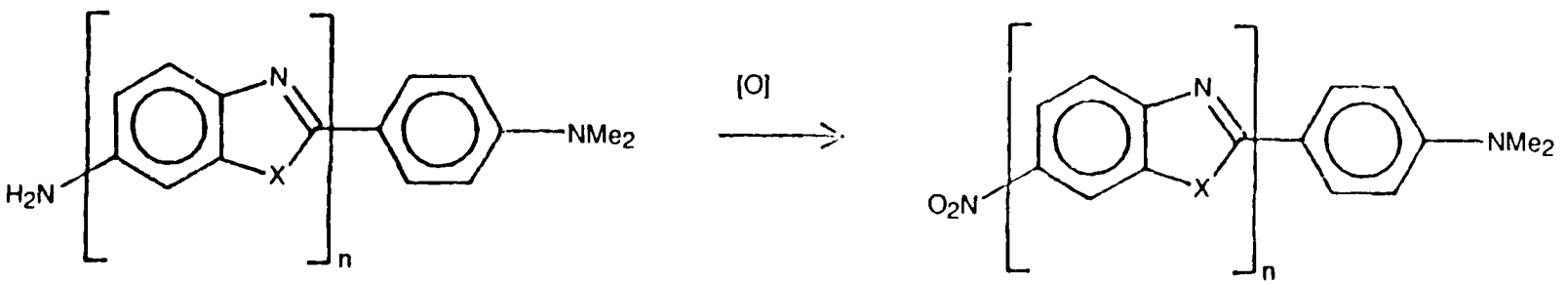

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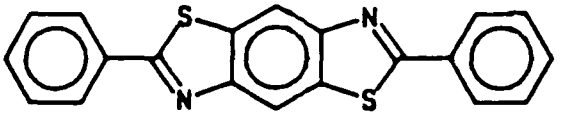
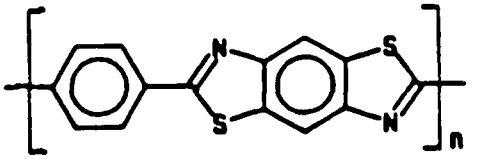
Figure 4 Preparation of compound 6.



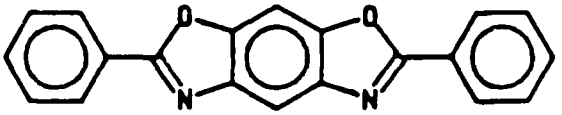
trans-BTZ

$x^{(3)} = 0.19 \times 10^{-12}$ esu

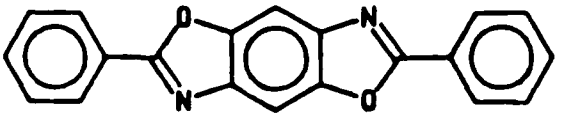


PBT

$x^{(3)} = 50\text{-}100 \times 10^{-12}$ esu



cis-BOZ



trans-BOZ

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Figure 5 PBT and PBO model compounds and PBT polymer.

11×10^{-36} esu, which agrees with the experimental value of 13×10^{-36} esu. These results indicate that the PBZ materials indeed offer the possibility for use in nonlinear optics.

Another product of our collaboration with Professor Garito has been the identification of specific organic compounds that have given calculated susceptibility values higher than available organic materials [for example, MNA (2-methyl-4-nitroaniline) or DANS (N,N-dimethylamino-4'-nitrostilbene)]. One of the prime candidates is compound 9, shown in Figure 6. The two cyano groups draw electron density from the terminal amines through the conjugated molecular structure. Similar diaminodicyano compounds of shorter conjugation length were originally synthesized from tetracyanoquinodimethane (TCNQ) and various amines.[5-7] Compound 9 is currently being synthesized by an eight-step route outlined in Figure 6. The reduction of 4-hydroxybenzoic acid was accomplished using hydrogen with Rh on alumina.[8]

The next step to form 2,6-di(4-hydroxycyclohexane)-benzo[1,2-d:4,5-d']bisthiazole (e) was attempted directly from 4-hydroxy-cyclohexanecarboxylic acid and DABDT in PPA. The product of this reaction was a yellow solid, that from the mass spectral, infrared, and elemental analysis results, suggested loss of the hydroxyl functionality. We will attempt this preparation by first substituting chloride for the hydroxyl groups of 4-hydroxycyclohexanecarboxylic acid to produce c which should be more stable to the condensation conditions. Conversion of the condensation product, d, to the dihydroxy compound, e, should proceed by hydrolysis with potassium hydroxide.

We have also conducted preliminary experiments to prepare a new polymer from the condensation of 4,6-diamino-1,3-benzenediol

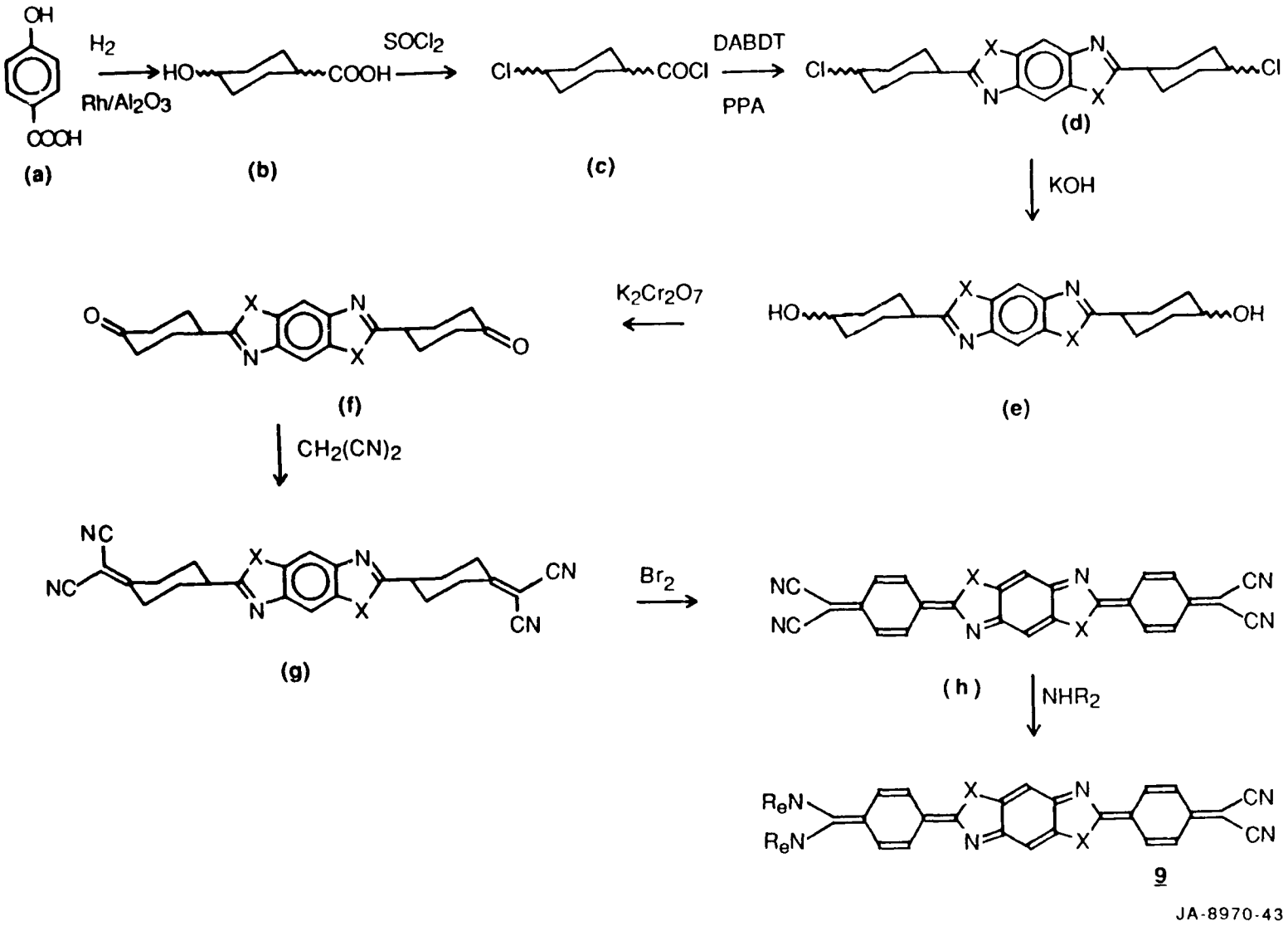

Figure 6 Preparation of quinodimethane analogs; compound 9.

dihydrochloride (DABDO) and squaric acid (3,4-dihydroxy-3-cyclobuten-1,2-dione). The expected product is the ladder polymer 10, Figure 3, that should exhibit interesting electrical and NLO properties. The product of the reaction was a black solid with low solubility, (including methanesulfonic acid) which prevented determination of the intrinsic viscosity. The material has thus far been prepared only as a black solid. Processing these and similar materials into useful forms will help to uncover their ultimate properties. One approach to this processing potential might involve the use of for example PBT as a template to align the ladder polymer.

EXPERIMENTAL PROCEDURES

2,6-Di(4-hydroxyphenyl)benzo[1,2-d:4,5-d']bisthiazole (1)

To a 300-ml resin kettle equipped with mechanical stirrer was added 31.79195 g (129.7 mmol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride and 172.5 g of PPA. The PPA was prepared by heating 704.94 g of 115% phosphoric acid with 251.71 g of 85% phosphoric acid to 120°C for 2 h under reduced pressure. The mixture was heated to 50°-55°C under reduced pressure until a clear solution free of HCl was obtained. To the solution was added 56.08014 g (406.0 mmol) of p-hydroxybenzoic acid and 124.91 g of P_2O_5. The mixture was heated at 95°-100°C overnight followed by heating at 180°-185°C for 16 h. The reaction mixture was quenched in water, neutralized with sodium hydroxide, filtered, washed with methanol and diethyl ether, and dried. Mass spectrum calc., 376; found, 377. Isolated yield 15.39 g (31%).

2-(4-Dimethylaminophenyl)-5-carboxybenzoxazole (2)

To a 100-ml resin kettle equipped with mechanical stirrer containing 10.41068 g (67.98 mmol) of 3-amino-4-hydroxybenzoic acid and 11.79055 g (71.37 mmol) of 4-dimethylaminobenzoic acid was added 58.15 g of a PPA solution that had been prepared by heating 42.839 g of 115% H_3PO_4 and 15.311 g of 85.3% H_3PO_4 to 120°C for 2 h under reduced pressure. To the mixture was added 39.2 g of P_2O_5 to give, after complete reaction, a final calculated P_2O_5 content of 84.7%. The reaction mixture was heated at 90°-95°C overnight. The reaction mixture was then heated to 160°C over 3 h and held at that temperature for 6 h.

The reaction mixture was quenched in water, filtered, and washed with methanol, yielding a green solid. Mass spectral analysis shows a major peak at 282 for the desired compound as well as minor peaks at 399 and 517 for the compounds with two and three repeat units, respectively.

2,6-Di(3-pyridyl)benzo[1,2-d:4,5-d']bisthiazole (3)

To a 100-ml resin kettle fitted with a mechanical stirrer was added 10.428 g (42.52 mmol) of DABDT and 36.54 g of a PPA solution prepared by heating under reduced pressure 107.85 g of 115% phosphoric acid and 38.55 g of 85.3% phosphoric acid. The mixture was heated under reduced pressure at 50°-60°C to remove the HCl. To the clear solution was added 10.793 g (87.67 mmol) of nicotinic acid and 24.49 g of P_2O_5 (the final calculated P_2O_5 content of the solution after condensation was 82.7%). The mixture was slowly heated to 170°-175°C and maintained for four hours. The reaction was quenched in water, washed with methanol, and dried. The product was recrystallized from toluene to give a 49% isolated yield. Mass spectrum calc., 346; found, 346. Anal. ($C_{18}H_{10}N_4S_2$): C, 62.41; H, 2.91; N, 16.17; S, 18.51. Found: C, 62.20; H, 3.18; N, 16.02; S, 18.96.

2,6-Di(4-dimethylaminophenyl)benzo[1,2-d:4,5-d']bisthiazole (4) n = 1

To a 100-ml resin kettle equipped with a mechanical stirrer was added 10.44168 g (42.59 mmol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and 37.06 g of PPA that was prepared by heating 107.85 g of 115% phosphoric acid and 38.55 g of 85.3% phosphoric acid to 120°C under reduced pressure for 2 h. The mixture was heated to 50°-70°C for 16-36 h under reduced pressure to reach a clear solution free

of HCl. To the solution was added 14.50025 g (87.88 mmol) of 4-dimethylaminobenzoic acid and 24.71 g of P_2O_5 to give a final calculated P_2O_5 content of 82.7%. The mixture was heated to 90°C for 3 h and then heated to 180°C over 1 h. The solution was heated at 180°-185°C for 16 h. The solution was quenched in water, filtered, and washed with methanol. Mass spectrum calc., 430; found 430.

1,4-Bis(5-nitrobenzoxazol-2-yl)benzene (7)

This compound was prepared by heating a ground mixture of 1.56582 g (7.71 mmol) of terephthaloyl chloride and 2.38075 g (15.45 mmol) of 4-nitro-2-aminophenol to 225°C under nitrogen flow for 16 h, producing a blue-black solid without melting. The product did not melt to 400°C. Mass spectrum calc., 402; found, 402.

1,2-Diamino-4,5-dinitrobenzene

This compound was synthesized according to the procedure of G.W.H. Cheeseman, J. Chem. Soc. 1170 (1962) by dinitrating N,N'-ditosyl-o-phenylenediamine in acetic anhydride by the action of 70% nitric acid, followed by removal of the tosyl groups with 86% sulfuric acid.

1,4-Bis(5,6-dinitrobenzimidazol-2-yl)benzene (8)

This compound was prepared by heating a ground mixture of 0.315 g (1.55 mmol) of terephthaloyl chloride and 0.520 g (2.62 mmol) of 1,2-diamino-4,5-dinitrobenzene to 225°C under nitrogen flow for 16 h producing a black solid without melting that was soluble in dimethylformamide (DMF) and purified by washing with DMF in a soxhlet

extraction apparatus to give a 70% yield of the DMF soluble product. Mass spectrum calc., 490; found, 490.

2-(4-Dimethylaminophenyl)-6-nitrobenzoxazole (5)

(Method 1): To a 100-ml resin kettle equipped with a mechanical stirrer was added 5.01971 g (30.3 mmol) of 4-dimethylaminobenzoic acid, 4.68296 g (30.4 mmol) of 4-nitro-2-aminophenol, and 82.38 g of 115% phosphoric acid. The mixture was heated at 60°-65°C overnight, then gradually heated to 150°C. The mixture foamed initially, suggesting loss of carbon dioxide. The mixture was quenched in water and washed with methanol then dried to yield a brown solid. Sublimation (0.1 mm, 150°-170°C) produced only a milligram quantity of a yellow solid. Mass spectrum calc., 283; found 283.

(Method 2): To a 100-ml resin kettle equipped with a mechanical stirrer was added 5.62712 g (34.1 mmol) of 4-dimethylaminobenzoic acid, 5.25085 g (34.1 mmol) of 4-nitro-2-aminophenol, and 72.35 g of a solution prepared from 29.04 g of P_2O_5 and 290.41 g of methanesulfonic acid. The mixture was heated at 135°-140°C overnight, evolving a small amount of gas. The reaction was quenched with water, yielding a brown solid. Extraction with DMF yielded 1.8 g of brown solid melting at 205°-208°C. Mass spectrum calc., 283; found, 283. Anal.($C_{15}H_{13}N_3O_3$): C, 63.60; H, 4.63; N, 14.83. Found: C, 63.41; H, 4.31; N, 14.84.

2-(4-Dimethylaminophenyl)-5-nitrobenzoxazole (6)

To a 100-ml resin kettle equipped with a mechanical stirrer was added 2.47959 g (15.0 mmol) of 4-dimethylaminobenzoic acid, 2.31361 g (15.0 mmol) of 5-nitro-2-aminophenol, and 40.76 g of 115% phosphoric

acid. The mixture was heated under argon flow at 65°-70°C overnight. The black mixture was then heated at 170°-175°C for 16 h. Carbon dioxide was liberated as indicated by an aqueous calcium hydroxide trap. The mixture was quenched in water and neutralized with sodium hydroxide, yielding 3.15 g of a brown solid (mp > 260°C). Mass spectrum calc., 283; found, nonvolatile.

2,6-Di(4-hydroxycyclohexane)benzo[1,2-d:4,5-d']bisthiazole

To a 100-ml resin kettle equipped with a mechanical stirrer was added 4.10 g (19.24 mmol) of 4,6-diamino-1,3-benzenediol dihydrochloride and 42.84 g of a phosphoric acid mixture that was prepared by heating 399.64 g of 115% phosphoric acid and 145.98 g of 85.8% phosphoric acid to 115°-120°C for 1-2 h under reduced pressure with stirring. The mixture was heated to 40°-50°C for 72 h under reduced pressure to eliminate the HCl. To the clear mixture was added 5.56 (38.57 mmol) of 4-hydroxycyclohexanecarboxylic acid and 18.47 g of P_2O_5. The mixture was heated at 145°-150°C for 16 h then at 165°-170°C for 2 h. The reaction mixture was quenched in water, neutralized with sodium bicarbonate, filtered, washed with water and methanol, and then dried under reduced pressure at 65°-70°C. The product was soluble in chloroform and acetic acid, melting at 215°-223°C. Infrared spectral analysis showed no indication of hydroxy functionality in the 3200-3600 cm^{-1} region. Mass spectrum calc., 384; found, 322, 341. Anal.($C_{20}H_{24}N_2O_4$): C, 67.39; H, 6.79; N, 7.86. Found: C, 69.85; H, 6.31; N, 7.75.

Polymers:

Dimethylamino Capped PBT (4)

To a 100-ml resin kettle equipped with a mechanical stirrer was added 11.67481 g (47.62 mmol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and 40.91 g of a polyphosphoric acid (PPA) solution prepared from 228.91 g of 115% phosphoric acid and 81.79 g of 85.3% phosphoric acid. The mixture was heated at 50°-70 °C under reduced pressure for 72 h to remove the HCl. To the clear yellow solution was added 7.87148 g (47.38 mmol) of terephthalic acid, 0.07720 g (0.632 mmol) of dimethylaminobenzoic acid, and 27.57 g of P_2O_5. The mixture is calculated to have a P_2O_5 content of 82.7% after polymerization. The reaction mixture was heated to 95°C for 16 h, followed by heating to 185°C over 2 h, then heating at 180°-185°C for 16 h. The capped PBT/PPA solution was stirred during the heating phase until the mixture rode on the stir blades. The mixture became yellow-green opalescent. Fiber samples were drawn from the solution, precipitated in water, washed with water, and dried at 160°-165°C. The intrinsic viscosity was measured at 16.6 dl/g in methanesulfonic acid at 30°C.

Squaric acid + DABDT (10)

To a 100-ml resin kettle equipped with a mechanical stirrer was added 9.26151 g (37.77 mmol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and 32.41 g of a polyphosphoric acid solution prepared from 226.01 g of 115% phosphoric acid and 80.25 g of 85.3% phosphoric acid. The mixture was heated at 50°-70°C under reduced pressure until a clear yellow solution free of HCl was obtained (72 h).

To the clear solution was added 4.30836 g of squaric acid (37.77 mmol) and 21.82 g of P_2O_5. When the yellow squaric acid was added to the clear yellow solution of DABDT, a green mixture resulted which became brown within 10 min of warming to 90°C. The mixture was stirred at 100°C for one week, followed by polymerization at 180°C for 24 h. During the polymerization, gas bubbles were evolved, indicating some decomposition. The black solid that resulted from quenching the mixture in water and neutralizing with sodium carbonate was sparingly soluble in methanesulfonic acid, making accurate determination of the intrinsic viscosity impossible.

INVENTIONS, PRESENTATIONS, AND PUBLICATIONS

The following invention was funded under this contract.

Invention Disclosure:

"Polymers and Oligomers for Nonlinear Optics," James F. Wolfe and Steven P. Bitler, Oct. 24, 1986.

Review Article:

J. F. Wolfe, "Polybenzothiazoles and Polybenzoxazoles," The Encyclopedia of Polymer Science and Engineering, 2nd Ed., Vol. 11 (J. Wiley & Sons, in press).

Presentations were given at the following conferences with the accompanying papers or briefs:

(1) J. F. Wolfe, "Stiff Chain Heterocyclic Polymers," International Symposium on Approaches to Property Limits in Polymers, Scanticon-Princeton, New Jersey, August 11-13, 1986.

(2) J. F. Wolfe, "Rigid Aromatic Heterocyclic Polymers for Nonlinear Optics," SPIE Conference, San Diego, CA, August 17-22, 1986.

(see Appendix D).

(3) S. P. Bitler and J. F. Wolfe, "New Synthesis," Air Force Ordered Polymer Meeting, Dayton, Ohio, October 28-31, 1986.

(4) A. W. Chow and J. F. Wolfe, "Dilute Solution Properties of Semirigid ABPBZ Polymers," Air Force Ordered Polymer Meeting, Dayton, Ohio, October 28-31, 1986.

(5) J. F. Wolfe, "Aromatic Heterocyclic Liquid-Crystalline Polymers: Synthesis, Properties, and Use in Molecular Composites," Thirteenth Biennial Polymer Symposium, Boca Raton, Florida, November 23-26, 1986.

(6) J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, A. F. Garito, S. P. Bitler and J. F. Wolfe, "Microscopic Origin of Third Order Properties of Rigid Rod Polymer Structures," XV International Quantum Electronics Conference, Baltimore, Maryland, April 27-May 1, 1987.

(see Appendix C).

(7) J. F. Wolfe and S. P. Bitler, "Rigid Aromatic Heterocyclic Polymers: Synthesis of Polymers and Oligomers Containing Benzazole Units for Electrooptic Applications," ACS Conference, Denver, Colorado, April 5-10, 1987.

(see Appendix A).

(8) A. W. Chow, P. E. Penwell, S. P. Bitler and J. F. Wolfe "Synthesis and Solution Properties of Some Extended Chain Poly(benzazoles)," ACS Conference, Denver, Colorado, April 5-10, 1987.

(see Appendix E).

(9) J. F. Wolfe and S. P. Bitler, "Aromatic Heterocyclic Stiff Chain Polymers," Regional ACS Conference, Columbus, Ohio, June 24-26, 1987.

(10) J. F. Wolfe, "Aromatic Heterocyclic Polymers," Interdisciplinary Symposium on Recent Advances in Polyimides and Other High Performance Polymers, Division of Polymer Chemistry, ACS Conference, Reno, Nevada, July 1987.

(11) A. W. Chow, J. E. Sandell and J. F. Wolfe, "Reaction Kinetics and Chemo-Rheology of Poly(p-phenylenebenzobisthiazole) Polymerization in the Ordered Phase," to be submitted to POLYMER, (see Appendix B)

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APPENDIX A

"RIGID AROMATIC HETEROCYCLIC POLYMERS:
SYNTHESIS OF POLYMERS AND OLIGOMERS CONTAINING
BENZAZOLE UNITS FOR ELECTROOPTIC APPLICATIONS"

To appear in American Chemical Society Proceedings

RIGID AROMATIC HETEROCYCLIC POLYMERS: SYNTHESIS OF POLYMERS AND OLIGOMERS CONTAINING BENZAZOLE UNITS FOR ELECTROOPTIC APPLICATIONS

James F. Wolfe and Steven P. Bitler

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

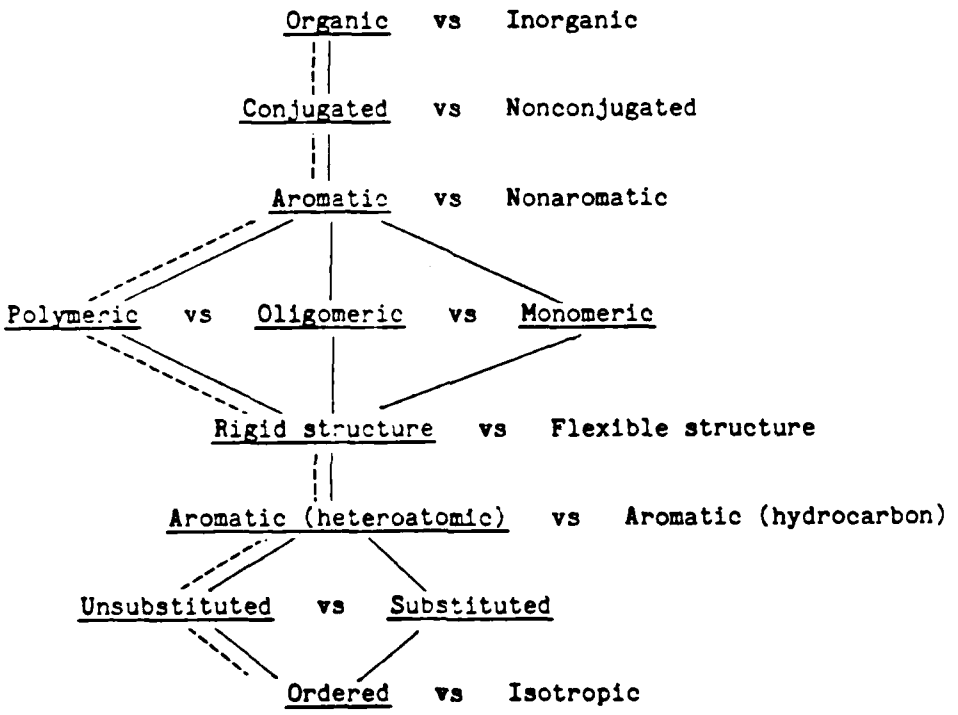
INTRODUCTION

Conjugated organic structures exhibit large, ultrafast nonlinear optical (NLO) responses that arise from excitation of highly charged correlated π-electron states. Highly aligned, high strength films of high molecular weight, rigid rod poly(benzobisazole) (PBZ) polymers have been shown recently to possess oustanding third-order NLO properties.[1,2] PBZ polymers, being comprised exclusively of aromatic rings, are conjugated structures with numerous possibilites for structural modification. In addition to ultrafast NLO response, PBZ polymers offer advantages of high damage thresholds, environmental stability, a wide variety of processing options, and excellent mechanical properties. Molecular structures with or without centers of symmetry can be prepared and the molecular weight distribution, electron density, and the molecular morphology can be varied over broad ranges. This tailorability in both molecular structure and supramolecular order provides promise for new materials with optimized NLO properties. This paper describes our recent work on the synthesis of PBZ polymers having controlled molecular weights. By controlling the molecular weight at relatively high levels, we aim to improve the processability and reproducibility of solutions for better optical quality high strength films. By preparing novel lower molecular weight materials, we aim to explore new structures that are specifically designed to maximize their NLO response and may require new methods for obtaining the high degree of molecular order that has become associated with PBZ materials.

Our polybenzazole synthesis research, which has been funded jointly by the Air Force Office of Scientific Research and the Air Force Materials Laboratory as part of the Air Force's Ordered Polymers Research Program, was originally aimed at materials for high performance structural applications. Our research focused initially on developing synthesis techniques to prepare particularly rigid polymer structures that would form lyotropic, liquid crystalline phases, when both the molecular weight and the solution concentration were above certain values. The basic synthesis methodology for preparing high molecular weight PBZ polymers has been described previously.[3,4] PBZ materials are prepared by condensation in poly(phosphoric acids) (PPAs) having high phosphorous pentoxide (P_2O_5) contents by an efficient process called the P_2O_5 Adjustment Method. The amount of P_2O_5 used depends on the concentration of the condensing species. This process

provides the basic condensation for the preparation of polymeric, oligomeric, substituted and unsubstituted PBZ materials.

Our efforts were expanded to include NLO applications when it became apparent that many of the same molecular design elements that resulted in thermal stability, high mechanical properties and orderability also led to desirable NLO properties.[5] The series of molecular design choices and morphological options shown in Scheme 1 illustrates the similarities between structural and NLO applications. To obtain maximum specific tensile properties and stability in a lightweight material for structural applications, the clear choices are those listed first on each line. Given the same choices for ultrafast NLO applications, the choices are clearly the same--except for those related to molecular weight and backbone substitution. The following two sections discuss the molecular design considerations relating to these two areas.



Scheme 1

Molecular Structure and Morphological Choices for Two Applications*

*High Strength Structural Applications ------
*Nonlinear Optical Applicatons ——————

Molecular Weight Considerations

The measurement of electron delocalization lengths in PBZ polymers by Dalton et al.[6] shows that delocalization does not extend beyond a few repeat units, even though the molecular structure is formally conjugated over the full length of the backbone. Because the NLO response is highly dependent on the electron delocalization length, we can view a high molecular weight PBZ polymer chain, in particular a rigid rod polymer chain, as a collinear string of separate NLO active sites. The question arises as to the role of the covalent links between the sites. Are they really necessary? They are clearly responsible for achieving nematic ordering, that

is, the additional dimension of order beyond the collinear one-dimensional array afforded by a single chain. Spontaneous formation of an anisotropic phase results if the molecular weight is above a critical value and the solution concentration is sufficient. The molecular weight required for obtaining good mechanical properties in films of PBZ polymers is much higher than the critical molecular weight required to obtain anisotropic (nematic) ordering. When rigid rod PBZ polymers are formed from monomer at high concentrations, such as 15 wt%, the degree of polymerization at which the nematic phase obtains is about 15 repeat units, corresponding to an intrinsic viscosity of 1.5 dL/g.

This second dimension of order, however, can also be obtained by poling small highly polarizable molecules, which do not obtain the nematic phase spontaneously at any achievable concentration. With the possibility of obtaining supramolecular order with rigid lower molecular weight molecules, we began to investigate methods of controllably reducing the molecular weight of PBZ materials having a "handle" for attachment to a flexible polymer backbone. In these efforts, good mechanical properties are desirable but are no longer the driving force behind the molecular design.

Substituent Effects

This portion of the current effort attempts to establish the synthesis goals for low molecular weight PBZ materials having electron-withdrawing and/or electron-donating substituents. The ultimate goal in this program is to establish the structure-property relationships that allow the design of optimized NLO materials. We have begun this effort by studying the effect of various substituted monofunctional reagents on the normal condensation in PPA.

RESULTS AND DISCUSSION

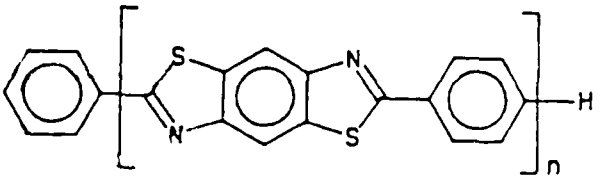
The five systems that address the above goals and will be described in this paper are listed in Figure 1.

PBT Polymers with Controlled Molecular Weights

Poly(*p*-phenylene-benzobisthiazole) (PBT) can be prepared with intrinsic viscosities as high as 48 dL/g by the condensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) with terephthalic acid in PPA. Chenevey has stated that the preferred range of PBT instrinsic viscosities for preparing films directly from PPA solutions, or dopes, is 20-30 dL/g.[7] A major goal of our synthesis research has been to define the variables of the PPA polymerization process sufficiently to allow not only the reproducible attainment of a specific intrinsic viscosity, but also control of all the key dope characteristics. The key dope characteristics, in addition to the molecular weight of the polymer, are the shear viscosity of the dope, and the morphology. The important synthesis variables to control are the DABDT purity, the concentration of the condensing species, the P_2O_5 contents during polymerization, and the amount of endcapping agent used.

We conducted a series of PBT polymerizations in which small percentages of benzoic acid were used as an endcapping agent. The percentage of benzoic acid, based on the molar quantity of DABDT employed, was varied from 0 to 1.0%. The equivalency of functional groups was maintained by reducing the molar amount of terephthalic acid by one-half of the molar amount of benzoic acid used. The final P_2O_5 contents of the dopes were maintained within the range determined previously to be optimal[3] and the polymer concentrations employed were either 12.5 or 15 wt%. The intrinsic viscosities of the PBT isolated from the dope were measured and the shear

A



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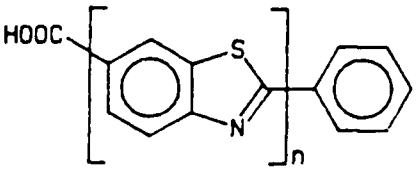

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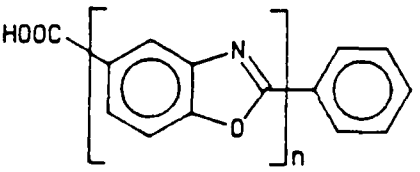

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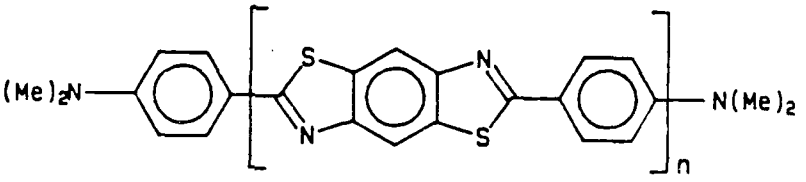

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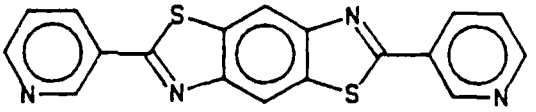

Figure 1. Chemical structures of (A) PBT, (B) ABPBT, (C) ABPBO, (D) p-dimethylaminobenzoic acid endcapped PBT, and (E) 2,6-di(3-pyridyl)-benzo[1,2-d:4,5-d']bisthiazole

viscosities of the dopes were determined. The experimental results are presented in Table 1.

The weight average molecular weights, Mw, were calculated from the intrinsic viscosities using the following relationship for PBT determined by Berry et al.:[8]

$$[\eta] = 1.65 \times 10^{-7} M_w^{1.8}$$

Flory's theory[9] for the depression of molecular weight by the nonequivalence of functional groups and the presence of monofunctional reagents was used to analyze the results. Flory defined the number average degree of polycondensation, X_n, as

$$X_n = \frac{1 + r}{2r(1 - p) + 1 - r}$$

where p is the extent of reaction of either of the functional groups, and r is defined as

TABLE 1
PBT ENDCAPPING STUDY

	Polymerization Conditions				Dope Properties			Theory	
Run No.	Endcapper %	r	Final P2O5 Content, %	PBT Conc., wt %	[η], dL/g	PBT Mw	Shear Viscosity poise/1000	p = 0.993 PBT Mw	p = 0.9945 PBT Mw
1	0	1	82.7	15	44	48,000	-	38,000	48,400
2	0.1	0.9995	82.9	15	30	38,800	76	36,700	46,300
3	0.2	0.9990	82.9	15	29	38,100	-	35,900	44,400
4	0.25	0.9988	82.9	15	27	36,600	-	35,000	43,500
5	0.5	0.9975	82.9	15	25	35,100	63		
6			82.7	15	29	38,100	78	32,300	39,500
7			82.7	15	26	35,800	48		
8	0.6	0.9970	82.9	15	20.5	31,400	34		
9			82.9	15	21.9	32,600	30	31,400	38,140
10			82.9	15	22.8	33,300	38		
11			82.9	15	23.1	33,500	38		
12	0.75	0.9963	82.7	12.5	15	26,400	-		
13			82.3	12.5	17	28,300	-	30,100	36,200
14			82.6	15	22	32,600	-		
15			82.4	15	24	34,300	-		
16	1.0	0.995	82.7	12.5	18	29,200	-	28,100	33,400
17			82.7	12.5	21	31,800	-		

$r = 200/[2[100-(\%\ endcap)/2]+2(\%\ endcap)]$

$[\eta] = 1.65 \times 10^{-7}[Mw]^{1.8}$

Shear viscosities were measured at 0.1 sec^{-1} at 175°C with a Brookfield RVT viscometer, Spindle #7

p = theoretical extent of reaction of either functional group

Theoretical Mw = 2 x 266.33(xn/2), assuming Mn = Mw/2, where

xn = number average degree of polymerization = $[1+r]/[2r(1-p)+1-r]$

$$r = \frac{\text{moles of A groups}}{\text{moles of B groups} + (2 \times \text{moles of C groups})} .$$

For these PBT polymerizations, the A groups are the ortho-mercaptoamino functions of DABDT, the B groups are the carboxyl functions of terephthalic acid, and the C groups are the carboxyl functions of benzoic acid.

Theoretical weight average molecular weights for two hypothetical cases can be calculated using Flory's equations, the appropriate values for r and assuming two extents of reaction, p, of 99.45% and 99.3%. These data and the experimental results are presented graphically in Figure 2. Nearly all the experimental results fall between the bounds defined by these two hypothetical cases, which indicates that polymerizations are fairly consistent in their effective extent of reaction. These data also show that the molecular weight is predicted to decrease by about 10,000, at r values near unity, for a decrease in the extent of reaction of only 0.15%.

The effective extent of reaction can be affected by many factors. First, impurities in either monomer could be the cause of a stoichiometric imbalance that would result not only in a lower extent of reaction but also in a lowered r value. Second, the extent of reaction could be lowered by the occurrence of side reactions, which could be caused by an improper heating schedule or an insufficient P_2O_5 content. We find that we achieve better reproducibility of results if the final P_2O_5 content of the polymerization is greater than 82.7% and preferrably 82.9% or higher. The shear viscosity is highly dependent on the P_2O_5 content. To maintain the shear viscosity at values less than 80,000 poise (at 0.1 sec^{-1}, 175°C) for

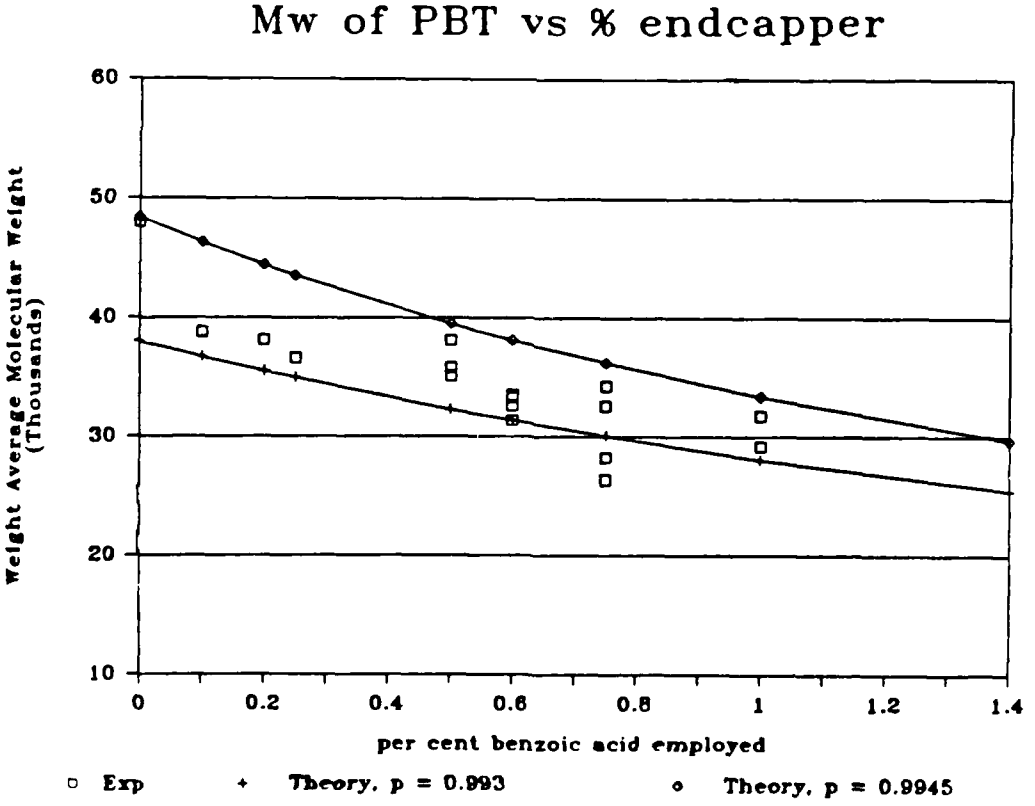

Figure 2. Weight average molecular weight of PBT versus percent benzoic acid endcapper used in the polymerization

intrinsic viscosities near 30 dL/g, the final P_2O_5 content of the dope must be kept below about 83%.

Early in this study, we noticed occasionally that the shear viscosities of the PBT dopes were abnormally high compared with other dopes having similar intrinsic viscosities, PBT concentrations, and final P_2O_5 contents. For example, the shear viscosities of runs 5 and 7 (see Table 1) should be nearly the same, based on these three variables. However, run 5 is 30% higher. We have attibuted the nonreproducibility of the shear viscosities to small amounts of disulfide impurities in the DABDT monomer that would become incorporated into the backbone of the otherwise rigid rod polymer. The presence of small amounts of such "articulated PBT polymers" in the anisotropic dope is expected to raise the shear viscosity dramatically. We spent considerable effort trying to detect this disulfide impurity in DABDT samples that gave high shear viscosities to confirm this assumption. Elemental analysis was not expected to be sensitive enough to detect low levels of this impurity. We used Raman and FTIR spectroscopy, but could not detect assignable differences between appropriate DABDT samples. We have indirect evidence that the cause of abnormally high shear viscosities is such a species, because normal shear viscosities were obtained from DABDT samples that were recrystallized under reducing conditions. This reductive recrystallization, which is described below, has become standard procedure in preparing DABDT of monomer grade purity.

Reproducibility of the shear viscosity and the intrinsic viscosity has been achieved by using DABDT monomer that has been recrystallized from stannous chloride/hydrochloric acid and by polymerizing at a concentration of 15 wt% and a final P_2O_5 content of 82.9%. Using these guidelines, PBT with an intrinsic viscosity of 23 dL/g can be obtained by replacing 0.3 mol% of the terephthalic acid with 0.6 mol% of benzoic acid.

Poly(benzazole) Polymers with High Levels of Endcapping

We also studied the effect of endcapping on the molecular weight of the two AB polymers, poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO). The percentage of endcapping agent was varied from 0 to 10%, which is a wider range than investigated in the PBT study. The experimental results are presented in Table 2. A theoretical extent of reaction was chosen for each experiment that gave a theoretical Mw, again using Flory's equations, that matched the observed molecular weight. One of the striking interpretations of this study is the apparent higher extent of reaction in ABPBO polycondensations relative to ABPBT. The extents of reaction of ABPBT are also higher than those believed to be operative in PBT polymerizations. We believe these interpretations are consistent with the electronic nature, which relates to relative oxidative stability, of the three monomers involved.

The weight average molecular weights of ABPBT and ABPBO were calculated from the experimentally determined intrinsic viscosities by using relationships derived by Chow et al.[10]

For 2,6-ABPBT, with Mw between 5,000 and 200,000

$$[\eta] = 1.256 \times 10^{-4} M_w^{1.00}.$$

For 2,5-ABPBO, within a similar molecular weight range

$$[\eta] = 1.089 \times 10^{-4} M_w^{1.02}.$$

TABLE 2
ABPBT AND ABPBO ENDCAPPING STUDY

	Experimental				Theory	
	% endcap	r	[η]	M_w	p	M_w
ABPBT Runs						
1	0	1	11.5	88,500	0.977	88,800
2	0.5	0.99	4.2	32,300	0.996	29,700
3	1.0	0.98	2.1	16,300	0.996	19,200
4	5.0	0.91	0.76	5,900	0.996	5,200
5	10.0	0.83	0.27	2,100	0.994	2,800
ABPBO Runs						
1	0	1	15.0	106,800	0.998	117,000
2	0.5	0.99	4.95	36,100	0.999	39,200
3	1.0	0.98	3.39	24,900	1.000	23,700
4	5.0	0.91	0.62	4,700	1.000	4,900

r = mol AB monomer/(mol AB monomer + 2 x mol of endcapper)
p = theor. extent of reaction = mol of A condensed/total mol of A

The plots of these equations and the relationships for the two rigid rod PBZ polymers, PBT and PBO, are shown in Figure 3.

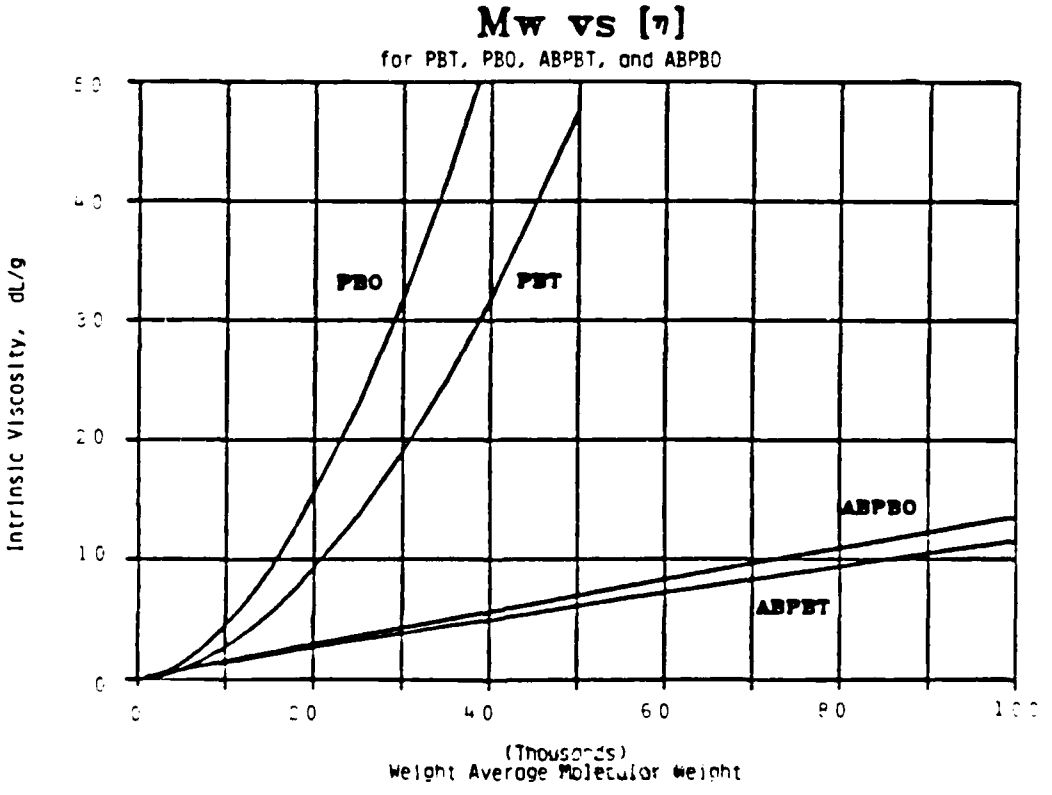

Figure 3. Weight average molecular weight versus intrinsic viscosity for PBT, PBO, ABPBT, and ABPBO

Preparation of Substituted PBZ Oligomers and Model Compounds

In addition to the above studies in which relatively minor percentages of benzoic acid were added to PBT, ABPBT, and ABPBO polymerizations, we have prepared PBZ materials using various functionalized endcapping agents. The goal is to determine the reactivity, stability, and compatibility of these compounds in the polymerizing medium to assess their usefulness in preparing PBZ materials with tailored electron densities and polarizabilities. By attaching a functional group to the end of a PBZ chain, the compound can either be synthetically modified after the PBZ portion of the molecule has been formed, or attached to the backbone of a common polymer. The material could also possibly be used directly in device fabrication.

We are investigating the following six functionalized endcapping agents:[11]

nicotinic acid (3-pyridinecarboxylic acid)
p-(N,N-dimethylamino)benzoic acid
4-nitrobenzoic acid
2-amino-5-nitrophenol
2-amino-4-nitrophenol
1,2-diamino-4,5-dinitrobenzene

Only the first two compounds allow the PPA polymerization of the oxidatively sensitive PBZ monomers to proceed without significant side reactions. The nitro-group containing compounds are believed to cause electron transfer from the electron-rich monomers under the PPA polymerization conditions leading to significant decomposition. Alternative synthesis methods may be required to introduce the nitro-group, such as a two-step procedure of oxidizing a nitro-group precursor.

Nicotinic acid has been used to prepare the dipyridyl benzobisthiazole model compound. Materials of this type have the potential for functionalization through the pyridyl nitrogen. Capping AB polymers with dimethylaminobenzoic acid gives a functionalized material that can be attached to polymer backbones directly through the terminal carboxyl group. The dimethylaminobenzoic acid endcapping agent gave results comparable with the results given for benzoic acid endcapping of DABDT. A PBT polymerization was conducted with 0.5 mol% of terephthalic acid replaced by 1 mol% of dimethylaminobenzoic acid. An intrinsic viscosity of 16.6 dL/g was obtained for the product.

Monomer Syntheses

Several advances have been realized during the current study in the synthesis of one of the important monomers used to prepare benzobisazole structures, namely 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT). The synthesis scheme for preparing DABDT, which is shown in Figure 4, is the same as that reported previously.[12] Several modifications have been found, however, to increase the yields and improve the reproducibility of the process. In the first step, p-phenylenediamine (PPD) dihydrochloride is dissolved in deaerated water and heated at 70°C with excess ammonium thiocyanate (NH_4SCN). We found that p-phenylenebis-(thiourea) (BTU), thus formed, is essentially void of the p-thiourea-aniline intermediate if the reaction temperature is decreased from 100°C to 70°C, the reaction time is increased to 48 h, and a sufficient excess of NH_4SCN is employed. The optimal ratio of NH_4SCN/PPD is 4.9/1 (mol/mol), which represents a 22.5% excess over the four moles required. The BTU formed under these conditions can be used in the next step without purification.

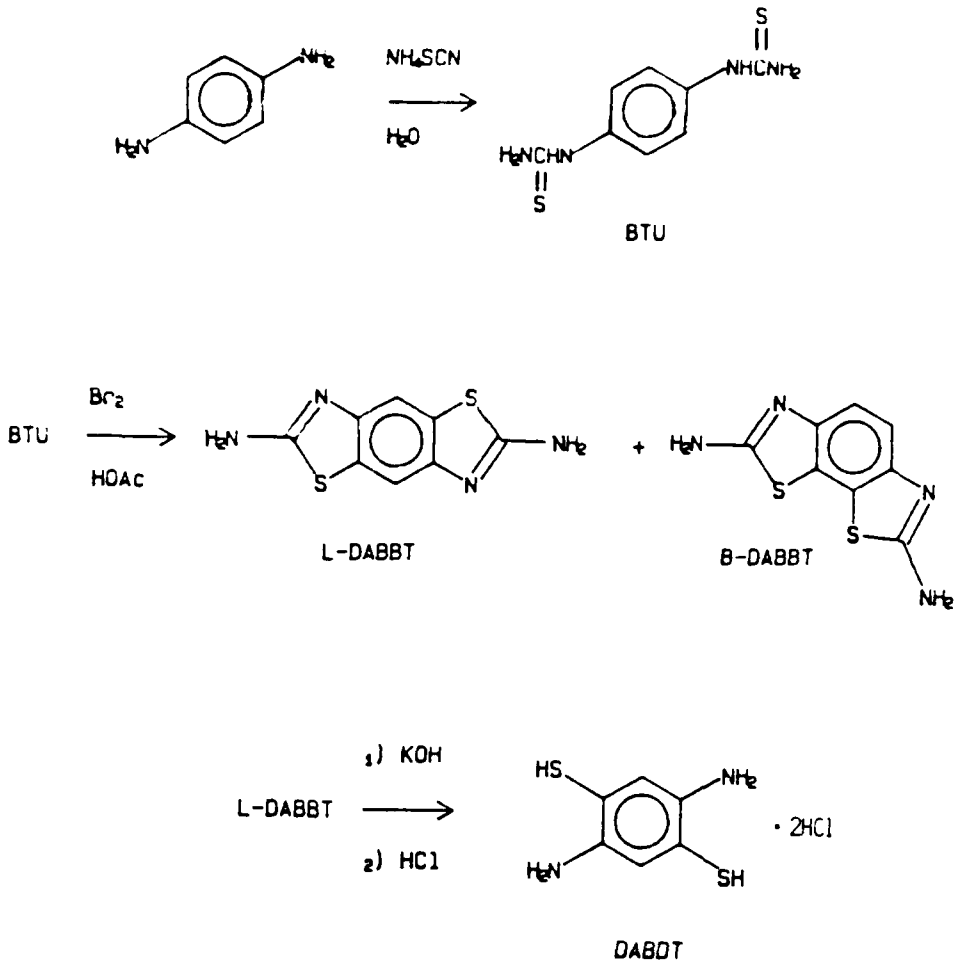

Figure 4. Synthesis of DABDT

The other modification of the published procedure is the addition of a hot stannous chloride recrystallization of the final product. This new procedure is described in the Experimental Section.

EXPERIMENTAL

Procedures

All intrinsic viscosities are reported in dL/g and are determined in distilled methanesulfonic acid (MSA) at 30.0°C by the extrapolation of reduced and inherent viscosities to zero concentration. Concentrations of the polymers are employed to give relative viscosities between 1.1 and 1.5.

Shear viscosities of dope samples were measured with a #7 spindle of a heavy duty Brookfield RVT Viscometer placed in a sample that had been immersed in an oil bath at 175°C.

Materials

Polyphosphoric acid (PPA). PPAs of various P_2O_5 contents are prepared by mixing commercially available 115% phosphoric acid (FMC) and 85% phosphoric acid (Baker Chemical Co.) and heating with stirring for 2 h at 115-120°C under reduced pressure.

MONOMERS

Terephthalic acid (TA). High purity TA was obtained from Amoco Chemical Co. and its particle size was reduced by an air impact method such that more than 95% of the particles were less than 10 μm.

2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT). Deaerated water (115 ml) was added to 27.5 g (0.124 mol) of 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole (DABBT) and 109 g (1.94 mol) of KOH in a 250 ml flask equipped with a reflux condenser and an overhead stirrer under inert atmosphere. The mixture was stirred and heated to 115-120°C for 7 h. The resulting clear amber solution was slowly cooled to 20-25°C overnight causing the dipotassium salt of DABDT to crystallize from solution. This white crystalline solid was collected by filtration under a carefully controlled nitrogen atmosphere, redissolved in 300 ml of deaerated water, and filtered under inert atmosphere into 300 ml of aqueous 37% HCl. The product was allowed to crystallize at least 6 h at 20-25°C then collected by filtration to yield 39 g of wet DABDT. The wet DABDT was recyrstallized in a reducing medium under inert atmosphere by adding the 39 g of wet DABDT to a hot (70-75°C) solution of 350 ml of water, 3.9 g of stannous chloride dihydrate, and 120 ml of aqueous 37% HCl. After stirring the solution for 5 min, 350 ml of deaerated water, preheated to 70-75°C, was added and the mixture was stirred at 70-80°C for 20 min to effect complete dissolution. The hot solution was filtered into 250 ml of aqueous 37% HCl causing immediate crystallization of the very light yellow DABDT. The product was allowed to crystallize at 10-20°C for at least 6 h and then collected by filtration. The DABDT was washed with methanol and then diethyl ether and then dried at 40-50°C under reduced pressure to yield 24.6 g (81%).

ENDCAPPING AGENTS

Benzoic acid, ACS reagent grade, was obtained from MCB Company and used as received.

p-(N,N-Dimethylamino)benzoic acid was obtained from Aldrich Chemical Company and recrystallized from toluene before use.

Nicotinic acid (3-pyridinecarboxylic acid) was obtained from Aldrich and used as received.

MODEL COMPOUNDS

2,6-Di(3-pyridyl)benzo[1,2-d:4,5-d']bisthiazole. A PPA solution was prepared by heating a mixture of 107.85 g of 115% phosphoric acid and 38.55 g of 85.3% phosphoric acid under reduced pressure for 2 h. DABDT (10.428 g, 42.52 mmol) was placed in a 100 ml resin kettle fitted with a mechanical stirrer and 36.54 g of the PPA solution was added. The mixture was heated at 50-60°C under reduced pressure to effect removal of the hydrogen chloride. Nicotinic acid (10.793 g, 87.67 mmol) was then added. P_2O_5 (24.49 g) was then added to give a calculated P_2O_5 content of the PPA of 82.7% after 100% of the theoretical condensation. The mixture was slowly heated to 170-175°C and maintained at that temperature for 4 h. The product was precipitated in water, washed with methanol and dried. The product was recrystallized from toluene to give a 49% isolated yield. Mass spectrum calc, 346; found, 346. Anal. ($C_{18}H_{10}N_4S_2$): C, 62.41; H, 2.91; N, 16.17; S, 18.51. Found: C, 62.20; H, 3.18; N, 16.02; S, 18.96.

POLYMERS

Dimethylamino capped PBT. DABDT (11.67481 g, 47.62 mmol) was placed in a 100 ml resin kettle equipped with a mechanical stirrer. A PPA solu-

tion (40.91 g), prepared from 228.91 g of 115% phosphoric acid and 81.79 g of 85.3% phosphoric aicd, was then added under a stream of dry nitrogen. The mixture was heated at 50-70°C under reduced pressure until a clear yellow solution was obtained (72 h). To the clear solution was added 7.87148 g (47.38 mmol) of terephthalic acid, 0.07720 g (0.632 mmol) of N,N-(dimethyl)aminobenzoic acid, and 27.57 g of P_2O_5. The mixture was calculated to have a P_2O_5 content of 82.7% after polymerization. The reaction mixture was heated to 95°C for 16 h followed by heating to 185°C over 2 h then heating at 180-185°C for 16 h. The capped PBT/PPA solution was stirred during the heated phase until the viscosity became so high that the mixture rode on the stirrer. The mixture became yellow-green opalescent. Fiber samples were drawn from the solution, precipitated in water, washed with water in a Soxhlet extractor, and dried at 160-165°C under reduced pressure. The intrinsic viscosity was measured to be 16.6 dL/g in methanesulfonic acid at 30°C. The bulk of the product was preserved as the liquid crystalline solution for subsequent processing.

Poly(2,6-benzothiazole) (ABPBT) with 1% Benzoic Acid Endcapper. A PPA solution (76.7% P_2O_5 content) was prepared by heating 20.04 g of 115% phosphoric acid and 9.07 g of 85% phosphoric acid at 100°C under reduced pressure for 2 h. A portion of this PPA (24.27 g) was added to a 100 ml resin kettle equipped with mechanical stirrer that contained 15.4 g (74.9 mmol) of 3-mercapto-4-aminobenzoic acid hydrochloride. This mixture was then heated at 65-70°C for 20 h to effect removal of the hydrogen chloride. To this solution was added 92 mg (0.75 mmol) of benzoic acid and 22.0 g of P_2O_5. The mixture was then stirred at 70-75°C for 2 h. The temperature was increased to 185°C over 6 h and maintained at that temperature overnight yielding 58.2 g of an opalescent golden-green ABPBT/PPA dope. The final dope was calculated to have an ABPBT concentration of 17 wt% and a P_2O_5 content of 83.0%. The intrinsic viscosity of fibers that were extracted with water and dried under reduced pressure at 160-165°C was 4.2 dL/g.

PBT Terminated with Benzoic Acid. A PPA solution, having a P_2O_5 content of 78.0%, was prepared from 247.17 g of 115% H_3PO_4 and 88.27 g of 85.3% H_3PO_4. DABDT (13.90951 g, 56.70 mmol) was added to a 100 ml resin kettle equipped with an overhead stirrer and then 47.97 g of the PPA was added. The mixture was heated at 50-70°C for 48 h under reduced pressure to effect elimination of the hydrogen chloride. To the clear yellow solution was added 9.40043 g (56.585 mmol) of terephthalic acid, 0.03471 g (0.2842 mmol) of benzoic acid, and 33.51 g of P_2O_5. The mixture was stirred at 90-95°C under inert atmosphere for 16 h. The yellow mixture was then heated to 180°C over a 1.5 h period and then heated at 180-185°C for 24 h. The resulting yellow-green opalescent PBT/PPA solution was calculated to be 15.0 wt% PBT and have a P_2O_5 content of 82.9%. Fibers were drawn from the solution, coagulated in water, washed with water in a Soxhlet extractor for 24 h, and dried at 160-165°C under reduced pressure for 8 h. The intrinsic viscosity in MSA was measured to be 25 dL/g. The shear viscosity of the PBT/PPA solution was 63,000 poise (0.1 sec^{-1}, 175°C).

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APPENDIX B

"REACTION KINETICS AND CHEMO-RHEOLOGY OF
POLY(P-PHENYLENEBENZOBISTHIAZOLE) POLYMERIZATION
IN THE ORDERED PHASE"

Submitted to POLYMER

REACTION KINETICS AND CHEMO-RHEOLOGY OF POLY(p-PHENYLENE-BENZOBISTHIAZOLE) POLYMERIZATION IN THE ORDERED PHASE

Andrea W. Chow, Janet F. Sandell, and James F. Wolfe

Polymer Sciences
Chemistry Laboratory
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

SYNOPSIS

The phenomenon of mesophase-enhanced polymerization of the rodlike polymer poly(p-phenylenebenzobisthiazole) at 15% by weight in polyphosphoric acid was investigated. The reacting mixture becomes anisotropic at early stage of the polymerization. The reaction rate increases significantly at the isotropic-nematic phase transition as the rods are aligned in positions more favorable for the condensation reaction to occur. The chemo-rheological properties at high shear rates ($\geq 10\ s^{-1}$), but not at low shear rates ($\leq 5\ s^{-1}$), also indicate the occurrence of the phase change. A systematic study of the effects of shear rate and temperature suggests that initial mixing of the monomer mixture below the polymerization temperature greatly influences the final achievable molecular weight of the polycondensation reaction.

Keywords: poly(p-phenylenebenzobisthiazole); rodlike polymer; mesophase-enhanced polymerization; reaction kinetics; ordered phase; chemo-rheology

INTRODUCTION

Polybenzazoles (PBZ), a class of aromatic, heterocyclic rigid rod polymers, have received increasing interest as advanced materials for applications requiring high thermal, oxidative, and structural stability. Because of the rigidity of the backbone, these polymers can form ordered phases in solutions at high chain concentrations. Such orderability has been known to provide great advantages to the polymer processibility and the physical properties of the fabricated products. Exceptional mechanical properties can be obtained in fibers and films fabricated from these lyotropic polymers. A tensile strength of 4.2 GPa (607,000 psi) and a tensile modulus of 330 GPa (48 million psi) have been reported for heat-treated fibers spun from poly(p-phenylene-benzobisthiazole) (PBT),[1] one of the most rigid polymers in the PBZ family.

Benefits can also be realized when polymer synthesis is performed in the ordered phase. Initial research on the synthesis of PBT was conducted in polyphosphoric acid (PPA) at concentrations below 3 wt% of polymers to avoid the extremely high shear viscosity of the reacting media. Such polymerization mixtures remained isotropic throughout the polymerization, but the maximum attainable molecular weight was low, and the polymer had to be isolated and redissolved at higher concentration for fiber processing. The practical need for higher efficiency motivated attempts to polymerize at higher concentrations. At greater

than 5 wt%, liquid crystalline domains were formed during the polymerization of PBT, and the reacting mixture remained tractible. The reaction kinetics and final attainable molecular weight were greatly enhanced. Moreover, the processibility of the dope was improved significantly.

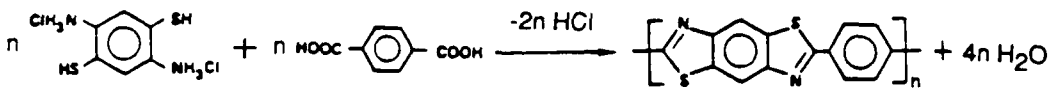
A study on the polymerization kinetics of another rodlike polybenzazole, poly(p-phenylenebenzobisoxazole) (PBO), at concentrations below the liquid crystalline phase transition indicates that the rate of increase in molecular weight with reaction time decreases with the molecular weight of the rodlike chains.[2] This result suggests that the polymerization rate is diffusion limited because the rotational diffusivity depends strongly on the molecular length. In the ordered phase, however, the molecules are already aligned in positions favorable for condensation, and the polymerization rate is therefore expected to increase. We call this phenomenon mesophase-enhanced polymerization (MEP).

Because of the scientific as well as technological importance of polycondensation of rodlike polymers in the ordered phase, investigated MEP in more detail. We describe a quantitative study on the reaction kinetics and chemo-rheological properties of PBT polycondensation at high concentration under conditions that cause liquid crystalline phase transition to occur during the polymerization. The effects of phase change, shear, and temperature are discussed.

EXPERIMENTAL

Material Preparation

The synthesis of PBT, reported in detail previously,[3] is typically performed by the condensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TA) in PPA following the removal of hydrogen chloride:



DABDT TA PBT

Preparation of DABDT monomers follows the rigorous purifying procedures described in the literature.[3] In all experiments, the monomer concentration is chosen to yield a final polymer concentration of 15% by weight. In this reaction, PPA serves as a solvent, catalyst, and dehydrating agent. Hydrogen chloride is first completely removed from the reaction mixture DABDT in PPA before the addition of 10 μm TA particles. Solid P_2O_5 is then added according to the P_2O_5 adjustment method[4] to ensure adequate reaction conditions for a high degree of polymerization. Benzoic acid of 0.50 mole% based on DABDT is used as endcapping agent to control the final molecular weight of the polymer.

After the original mixture of DABDT and PPA at 90°C is stirred for sufficient time to remove the hydrogen chloride, the mixture of monomer, benzoic acid, PPA, and P_2O_5 is ready for polymerization at temperatures above 150°C.

Polymerization Kinetics

Most of the polymerization runs in this study follow a temperature profile known to produce satisfactory conditions for the polymerization. The monomer mixture is first heated from 90°C to 180°C at a rate of 0.75°C/min. When the mixture reaches 180°C, the temperature is maintained at 180°C throughout the polymerization. In a few cases, different temperature profiles are used to investigate their effects on the reaction.

All monomer mixtures are prepared in 500-mL glass reactors with three attached ground glass joints. This reactor design allows constant mechanical stirring of the reaction mixture and continuous argon purge. During polymerization, small aliquots of the reaction mixture are removed periodically from the glass reactor. The reactor also allows removal of samples for analysis without exposing the reacting mixture to air or introducing other contaminants. A heated oil bath is used to control the reactor temperature.

A portion of the removed aliquot is placed on a microscope slide for direct observation under an optical microscope. The remaining portion is precipitated in deionized water, and the residual PPA is

thoroughly removed by extraction with water in a Soxhlet apparatus. The polymer is completely dried under reduced pressure at >130°C overnight.

The weight-average molecular weight, M_w, of PBT can be determined by measuring the intrinsic viscosity of the polymer in dilute concentrations and using the following Mark-Houwink relationship:[5]

$$[\eta] = 4.86 \times 10^{20} \, (d_H^{0.2}/M_L) \, (M_\eta/M_L)^{1.8} \quad (1)$$

$$M_\eta = M_w \, (M_z/M_w)^{4/9} \quad (2)$$

The intrinsic viscosity $[\eta]$ is in dL/g; d_H is the hydrodynamic diameter of a chain element taken to be 7×10^{-7} cm for PBT; M_L is the mass per unit length, which is 2.15×10^9 cm^{-1}; M_z is the z-average molecular weight, and M_z/M_w is 1.3 for PBT.

Experimentally, the intrinsic viscosity of PBT solutions is measured at 30.0°C using an automated Cannon-Ubbelohde microdilution viscometer. The solutions are prepared by dissolving dried PBT in freshly distilled methane sulfonic acid (MSA), and the intrinsic viscosity is measured within 48 hours after the solutions are prepared. Four successive dilutions are used for extrapolating the measurements of specific and inherent viscosities to infinite dilution. The solution efflux times are chosen to fall within 1.1 to 1.5 times the solvent efflux time. No kinetic correction is necessary because the efflux times are longer than 100 s.

Rheology

Rheological measurements on the polymerizing mixtures are performed using a Rheometrics RMS-605 mechanical spectrometer. Because of the high sensitivity of the reaction mixtures to oxygen and moisture, a modified cone-and-plate fixture is used to prevent exposure of the reacting mixture to moisture over a long period (at least several hours). The fixture, made of Hastelloy C to resist acid corrosion at elevated temperature, consists of additional outer, concentric rings on both the cone and the plate such that dried, high-temperature-grade silicone oil can be introduced to form a barrier to moisture and oxygen as shown in Figure 1. The diameter of the plate is 25 cm and the cone angle is 0.1 radian.

About 1 mL of the prepared monomer mixture at 90°C is removed from the bulk sample under nitrogen purge and loaded onto the cone-and-plate fixture carefully to minimize contaminant introduction. The flow cell is preheated to 90°C to avoid reprecipitation of the dissolved components. The sample is kept under a nitrogen blanket until the flow cell is closed and sealed with silicone oil. The temperature of the sample is then increased according to a predetermined temperature profile to initiate the polymerization. Different temperature profiles have been followed to investigate the effect of temperature on the polymerization.

The effect of shear is studied by subjecting the polymerizing media to continuous steady shear throughout the reaction (including the

initial temperature ramp) at shear rates from 0.01 s^{-1} to 50 s^{-1}. The rheometer is programmed to record the torque reading and calculate the shear viscosity at about two-minute intervals. At the end of each run, the dope is removed from the flow cell for molecular weight determination using intrinsic viscosity measurements.

After a series of polymerization runs, the remaining bulk monomer mixture is polymerized in the glass reactor using a similar temperature profile for comparison purposes.

RESULTS AND DISCUSSIONS

Polymerization Kinetics

Figure 2 shows the change in the intrinsic viscosity as a function of reaction time of 15 wt% PBT in PPA. The dotted line shows the temperature profile throughout the reaction starting from 150°C. The intrinsic viscosity can be converted to the weight-average molecular weight (M_w) using Eq. (1). The number-average degree of polymerization (x_n) can then be determined by the molecular weight of the repeat unit (M_o) and M_w:

$$x_n = 2(M_w/1.3M_o) \tag{3}$$

The factor of 2 is needed because two condensing species form each repeat unit. The constant 1.3 within the parenthesis is used to convert weight-average to number-average molecular weight by assuming a polydispersity of 1.3.[2,6] Figure 3 plots x_n as a function of reaction time.

The salient feature of Figures 2 and 3 is the sharp increase in the intrinsic viscosity and x_n at about 40 minutes (t_1) after time $t = 0$ at 150°C. The slope of the curve immediately following t_1 is increased significantly. Figure 4 shows the rate of polymerization, $d(x_n)/dt$, which is calculated from the slope of the curve in Figure 3 at the midpoint between data points. More than a five-fold increase in the

polymerization rate is observed at the transition. In contrast, polycondensation of PBO at low concentrations (below 2 wt%) exhibits only a decreasing rate of polymerization with increasing molecular weight throughout the entire reaction.[2]

Direct observation indicates that, at the same time that the kinetic rate increases abruptly, the reacting dope becomes stir-opalescent, indicating the onset of a liquid crystalline phase in the dope. Analysis of thin samples under a polarized optical microscope shows that the dope is birefringent at $t \geq t_1$ but isotropic at $t < t_1$. The abrupt increase in the reaction rate is therefore interpreted as a quantitative description of the mesophase-enhanced polymerization by which the enhancement in kinetics is due to the alignment of rigid rods in the ordered phase.

It is coincidental that t_1 appears very close to the point at which the temperature reaches 180°C. We suspect that the abrupt increase in the kinetic rate is a result of the temperature profile and not due to the phase transition. However, previous study on polycondensation of PBO in the isotropic phase does not indicate any discontinuous change in the polymerization rate with temperature from 150° to 185°C.[2] Therefore, the observed change in the kinetics is too dramatic to be due to the gradual increase in temperature as performed in our experiments.

The polymer molecular weight at which the phase transition occurs can be compared with theoretical predictions using Flory's statistical

mechanical model for athermal systems.[7] The model predicts that ϕ_c, the critical volume fraction of rodlike solute at which phase separation first occurs, is related to the axial ratio (x) of monodisperse rods by

$$\phi_c = (8/x)(1 - 2/x) \qquad (4)$$

In our polymerization of PBT, the specific gravity of PBT is about 1.5 and that of PPA is 2.0. ϕ_c is therefore 0.19 and x is 40 according to Eq. (4). Experimentally, we observed a phase change when the number-average molecular weight of PBT is less than 6016 dalton. If we assume 0.7 nm to be the molecular diameter of PBT, and 1.25 nm to be the length of a repeat phenylenebenzothiazole unit based on crystallographic results on model compounds,[8] the critical number-average axial ratio of PBT is calculated to be less than 40 ($x_n = 45$) when the phase transition was first detected. Our experimental result compares favorably with the theoretical value.

Flory's theory also predicts a wholly anisotropic phase to occur when $x = 12.5/\phi$ for a monodisperse system. Calculations based on this model indicate a narrow bisphasic region, with a complete nematic phase at $x = 66$ ($x_n = 73$) for PBT. Although a broader biphasic region is expected for polydisperse systems,[9] the rapid polymerization rate at 180°C makes it difficult to accurately determine the breath of the biphasic region.

Figure 4 suggests that, in the liquid crystalline phase, the polymerization rate versus reaction time can be empirically described by an exponentially decaying function, and the degree of correlation of such curve fitting is 0.99. The decrease in the rate of polymerization is a function of the amount and reactivity of endcapping agent, the reactivities of side reactions, and possibly the molecular weight of the polymers. More research is needed to better understand the physical significance of such exponential dependence.

Chemo-Rheological Properties

The rheological behavior of lyotropic, rigid rod macromolecules near the isotropic-nematic phase transition has been a subject for numerous theoretical as well as experimental investigations.[10] In most experimental studies, the shear viscosity is measured as a function of concentration at a fixed molecular weight and temperature. Characteristically, the viscosity first increases with concentration, reaches a maximum near the phase transition, then decreases in the nematic phase region at high concentrations.

In the PBT polymerization, the volume fraction of rods stays constant while the molecular weight and the temperature vary with time. The shear viscosity of the reacting media, monitored by the rheometer in cone-and-plate geometry, is shown in Figure 5 for shear rates of 1, 5, 10, and 50 s^{-1}. The temperature profile in these experiments follows that in the kinetic study described in the last section: an increase of

0.75°C/min from 90° to 150°C, followed by a hold at 180°C throughout the remaining time of the reaction.

In all the experiments shown in Figure 5, the specified shear was applied starting from 90°C. Previous experience indicates that no appreciable reaction can be detected until the temperature reaches at least 150°C; data acquisition therefore begins at 150°C. At shear rates of 1 s^{-1} and higher, the resulting dopes at the end of all runs appear green and stir-opalescent, and it is easy to draw long fibers from the dope. These are indications of moderately high molecular weight polymers in the ordered phase.

To our surprise, the rheological data at low shear rates (1 and 5 s^{-1}) provide little indication of the isotropic-nematic phase transition. The viscosity increases monotonically and quite smoothly with reaction time. At higher shear rates (10 and 50 s^{-1}), a slight break in slope in the viscosity function near 40 to 50 minutes is observed. This break is very close to, and therefore suspected to be related to, the phase transition observed in the kinetic study.

In Figure 5(a) and (b), the viscosity increases very slowly or levels off at long reaction time. Figure 5(c) and (d), however, exhibit more unusual features beyond the phase transition. Figure 5(c) shows a dip in viscosity at 81 minutes. Figure 5(d) shows a dip at 66 minutes, followed by a dramatic drop in viscosity after 90 minutes. The origins of these sudden reductions in viscosity are unclear. Some may be due to changes in the degree of order in the nematic phase, and some may be

artifacts resulting from secondary flows, sample slippage, or sample being spun out of the flow cell due to the high rotational rate of the cell. Without further experimental evidence, we believe that the decrease is unlikely to be a manifestation of the biphasic-nematic phase transition.

Polymerizations performed at shear rates below 1.0 s^{-1} were less successful than those at higher shear rates. At 0.1 s^{-1}, the final greenish dope shows poor fiber-forming properties. Below 0.1 s^{-1}, the final material appears brownish-orange with black streaks, and no fiber can be drawn. Such appearance suggests low molecular weight materials. Figure 6 illustrates the intrinsic viscosity of the final dope versus the shear rate at which the polymer is polymerized. This figure suggests that the shear rate has significant effects on the final molecular weight.

We also observe that the degree of polymerization of PBT polymerized in the cone-and-plate cell is significantly less than those polymerized in the glass reactor. The same batch of monomer mixture polymerized in the glass reactor after the series of shear experiments were conducted yields an intrinsic viscosity of 16.7 dL/g; no higher than 13 dL/g is obtained in the rheometer as shown in Figure 6. This discrepancy may be due to one or more of the following: (1) contaminants (e.g., oxygen, moisture) introduced during loading of the monomer mixture onto the rheometer, (2) contaminants on the surface of the flow cell, (3) surface effects of the flow cell, and (4) differences in

monomer mixing in early stages of the polymerization. However, this problem does not invalidate our earlier observation that the phase change effect does not seem to manifest itself in the low shear viscosity function since the final dopes from the rheometer are indeed liquid crystalline.

The shear dependence on the final degree of polymerization could be a result of an enhancement in molecular alignment during shearing, or simply better mixing of the monomer mixture or the reacting medium. To distinguish between these two possible mechanisms, we performed two experiments in which a combination of shear rates was used. In one polymerization run, the monomer mixture was first sheared at 1 s^{-1} from 90° to 150°C, and the shear rate was reduced to 0.01 s^{-1} starting at 150°C throughout the polymerization. This shear profile yielded polymer with a final intrinsic viscosity of 11.2 dL/g, although the shear rate of 0.01 s^{-1} alone has been found to be inadequate to achieve successful polymerization. In a second polymerization run, a shear rate of 0.1 s^{-1} was applied below 150°C and 10 s^{-1} above 150°C, and the resulting polymer exhibited an intrinsic viscosity of only 7.9 dL/g. These results suggest that a mixing effect, not molecular alignment, is the underlying reason for the shear dependence of the degree of polymerization.

Figure 7 illustrates the results on final intrinsic viscosity versus shear rates used for polymerizing the monomers. The arrows indicate the direction of change in shear rate at 150°C. Good

correlation with previous polymerization results can be obtained when the initial shear rates, not the final ones, are used in a plot of the intrinsic viscosity versus shear rate.

We investigated the effects of different temperature profiles on the polymerization at a constant shear rate of 1 s^{-1}. Figure 8 shows three profiles. In the first one, described previously, the final PBT shows an intrinsic viscosity of 10.0 dL/g. The second profile shows a sharp increase from 90° to 180°C in 20 minutes, and we only found a brownish-black residue, which appears to be a degradation product of the monomer at the end of the polymerization. The third profile contains an increase from 90° to 150°C in 20 minutes, a hold at 150°C for 100 minutes, and a sharp increase from 150° to 180°C. This profile produced the best results, a final polymer intrinsic viscosity of 12.6 dL/g, which is one of the highest obtained among all polymerization runs performed in the rheometer.

These data indicate that the temperature profile during the mixing period below 150°C has a drastic influence on the polymerization, whereas the temperature profile above 150°C has less effect on the resulting product. The results on the temperature and shear rate studies can be explained by a rapid polymerization for which an intimate mixture is critical and by the decreased sensitivity of oligomeric species to thermal decomposition.

CONCLUSIONS

This study demonstrates quantitatively the enhancement in the polymerization kinetics of PBT when ordered domains form in the polymerizing solution. Chemo-rheological measurements at low shear rates throughout the polymerization, however, are a poor indication of the dramatic change in the reaction rate due to the phase change. At higher shear rates, the viscosity function exhibits features believed to be resulting from the phase transition. Moreover, at long time and high shear, the viscosity displays characteristics that have uncertain origins. These results are difficult to simulate by model study because the shear viscosity is a complicated function of the temperature, molecular weight, P_2O_5 content, shear rate, and the degree of order in the nematic phase. Currently, there is no satisfactory unified theory on the rheology of rodlike polymers that can account for these complicated effects

The shear rate and temperature effects on the polymerization products were not anticipated. Our data indicate that these parameters are most influential in the premixing stage (below 150°C) and much less influential in the polymerizing stage (above 150°C). Such results suggest that, once the monomer mixture is well dispersed initially, the polymerization can be performed to satisfaction under a wide range of reaction conditions. Conversely, if good mixing is not achieved in the early stage when the viscosity is low, later mixing is much less

effective after PBT starts to polymerize significantly. We suspect that the dissolution of TA particles may be the limiting step to good mixing in the early stage.

Several unanswered questions have risen in this study. We have not yet been able to resolve the discrepancy in the final degree of polymerization between the glass reactor and rheometer runs. We are now investigating the possible effects of contamination and flow cell geometry.

ACKOWLEDGMENT

We gratefully ackowledge the funding support of the Air Force Office of Scientific Research, contract number F49620-85-K-0015, for this research. We also thank Dr. Steve Bitler and Mr. Robert Sanderson for material preparation and their assistance in the kinetic experiment, and Mr. Paul Penwell for performing some of the intrinsic viscosity measurements.

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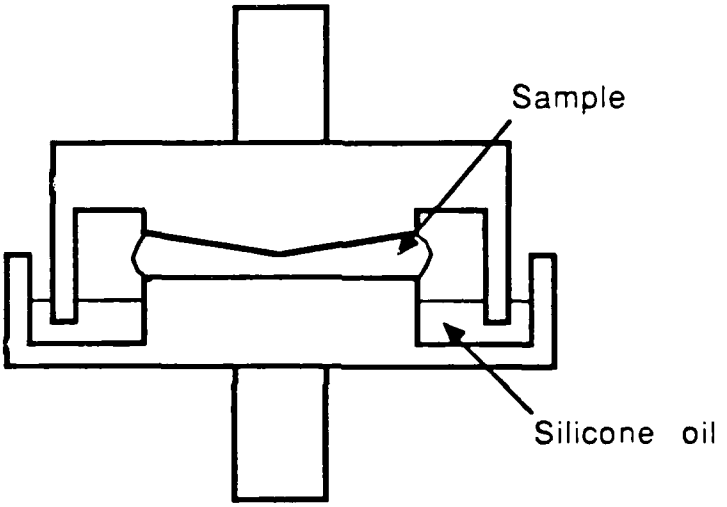

JA-8970-30

Figure 1 Modified cone-and-plate with moisture seal.

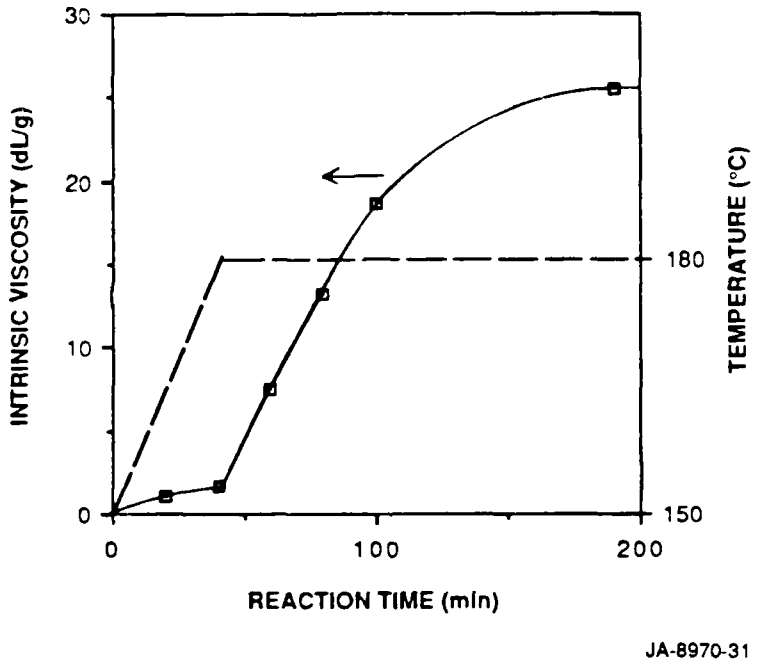

Figure 2 Increase in polymer intrinsic viscosity during polycondensation of 15 wt% PBT in PPA.

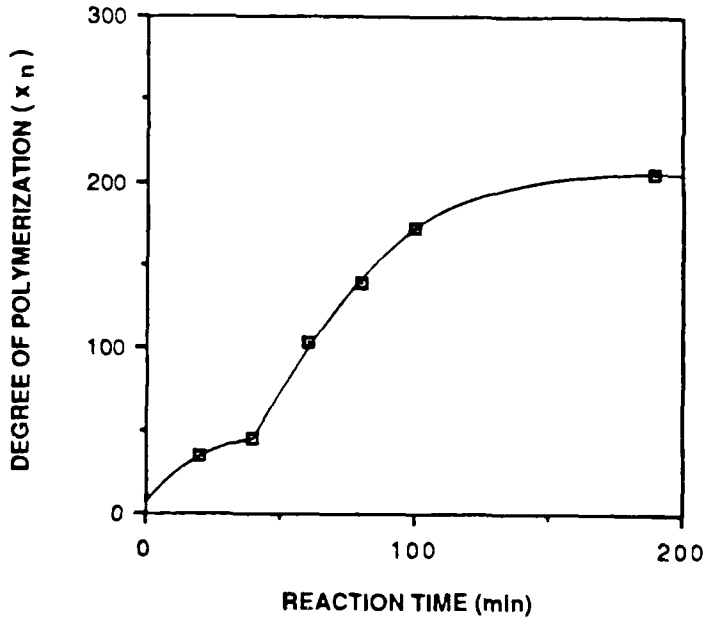

Figure 3 Degree of polymerization as a function of reaction time for polycondensation of 15 wt% PBT in PPA.

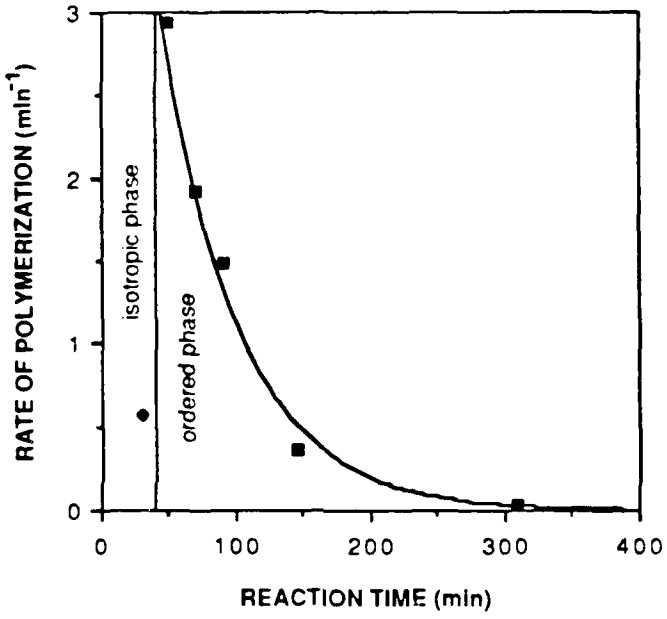

Figure 4 Rate of polymerization as a function of reaction time for polycondensation of 15 wt% of PBT in PPA.

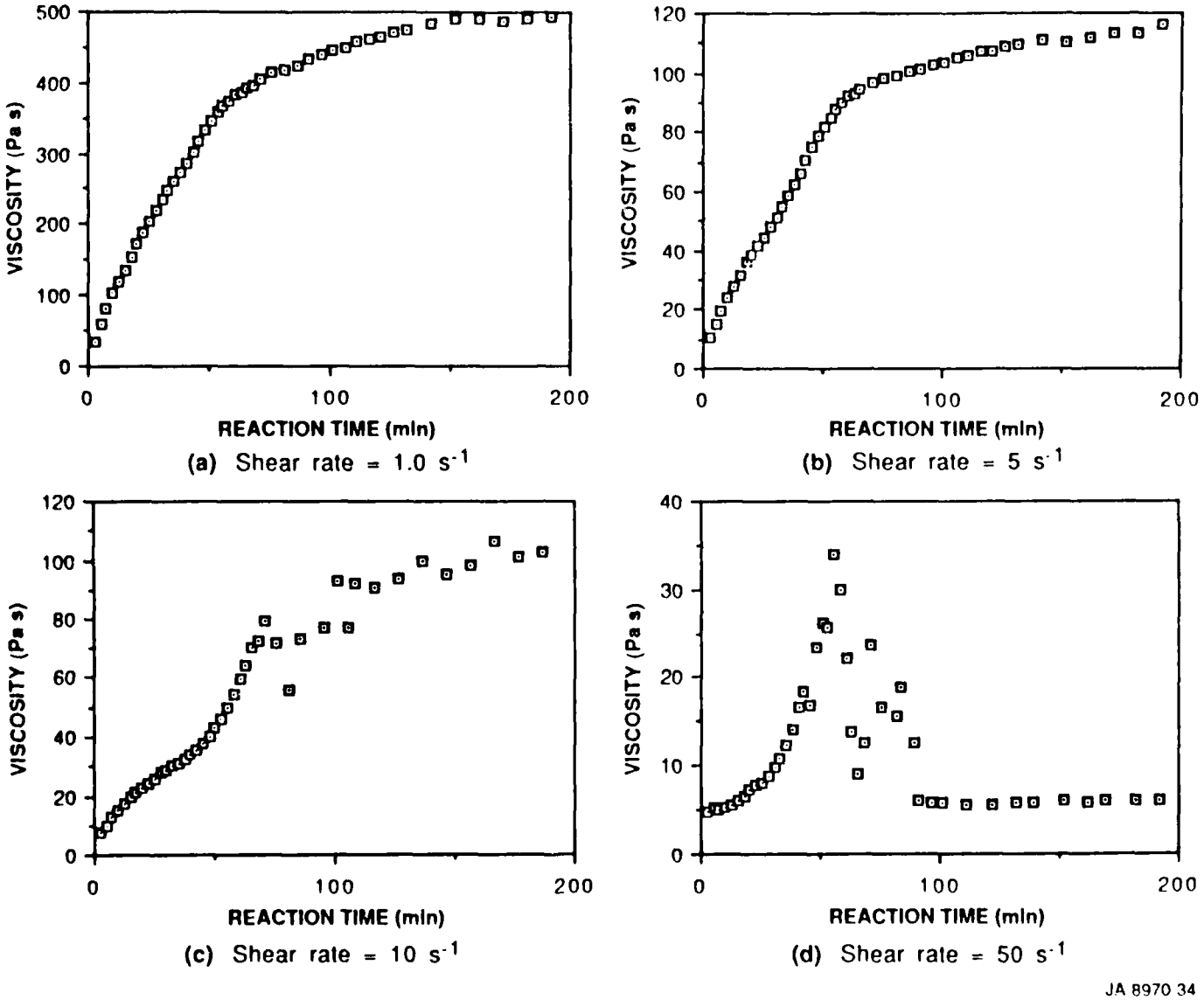

Figure 5 Shear viscosity versus reaction time during polymerication of 15 wt% PBT in PPA at shear rates 1.0 s^{-1}, 5.0 s^{-1}, 10 s^{-1}, and 50 s^{-1}.

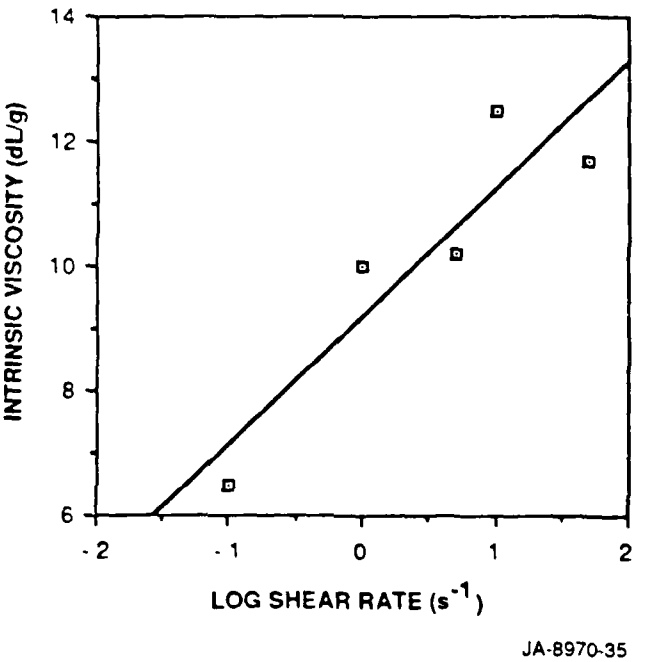

Figure 6 Semilogarithmic plot of the final polymer intrinsic viscosity versus the shear rate used for the polymerization.

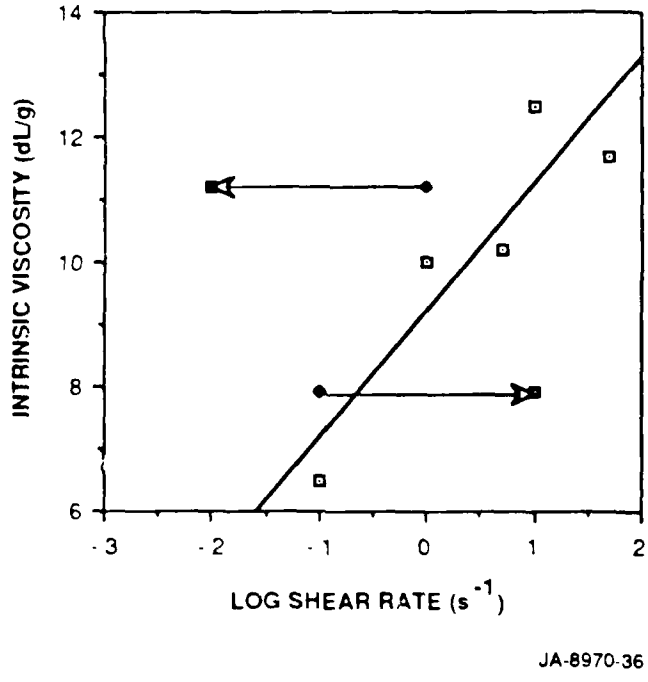

Figure 7 Semilogarithmic plot of the final polymer intrinsic viscosity versus the combination of shear rates used for the polymerization.

The arrows indicate direction of shear rate change at 150°C.

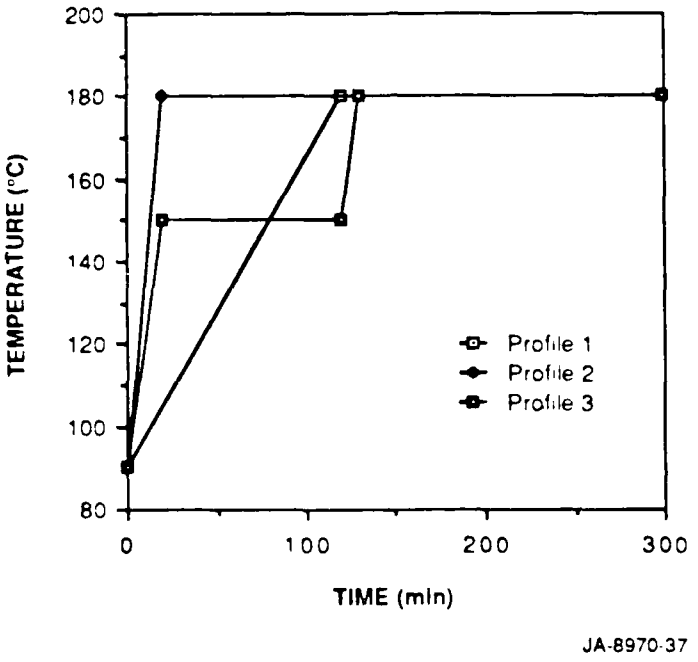

Figure 8 Three temperature profiles used for polymerizing 15 wt% PBT in PPA.

APPENDIX C

"MICROSCOPIC ORIGIN OF THIRD ORDER PROPERTIES
OF RIGID ROD POLYMER STRUCTURES"

Conference Abstract

Microscopic Origin of Third Order Properties of Rigid Rod Polymer Structures

J.R. Heflin, K.Y. Wong, O. Zamani-Khamiri and A.F. Garito
University of Pennsylvania
Department of Physics and
Laboratory for Research on the Structure of Matter
Philadelphia, PA 19104-6396
(215-898-5810)

S.P. Bitler and J.F. Wolfe
Polymer Science Department
SRI International
Menlo Park, CA 94025
(415-326-6200)

Abstract

Through experimental and theoretical studies, the microscopic origin of third order responses $\gamma_{ijkl}(-3\omega,\omega,\omega,\omega)$ of rigid rod polymer structures is found to be determined by virtual excitations to highly correlated two photon ^1A_g π-electron states and the first principal one photon ^1B_u excited state

Microscopic Origin of Third Order Properties of Rigid Rod Polymer Structures

J.R. Heflin, K.Y. Wong, O. Zamani-Khamiri and A.F. Garito
University of Pennsylvania
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Laboratory for Research on the Structure of Matter
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S.P. Bitler and J.F. Wolfe
Polymer Sciences Department
SRI International
Menlo Park, CA 94025
(415-326-6200)

Summary

Organic and polymer structures exhibit large, ultrafast second and third order nonlinear optical properties due to highly charge correlated π-electron excitations. Rapid advances in the field are being achieved through development of high strength polymer structures possessing both outstanding primary nonlinear optical properties and secondary structural properties as recently demonstrated, for example, in high performance rigid rod PBZ [poly(benzbisazole)] polymer structures[1,2]. Since each rigid rod polymer chain is essentially a densely packed, linear array of linked monomer units, a repeat unit can be viewed as the finite chain limit to the corresponding infinite polymer chain. Accordingly, we report experimental and theoretical studies of the microscopic third order susceptibilities

$\gamma_{ijkl}(-\omega_4;\omega_3,\omega_2,\omega_1)$ of centrosymmetric TBOZ and TBTZ repeat unit structures of PBZ polymers (Figure 1).

The nonresonant macroscopic third harmonic susceptibility $\chi_L^{(3)}(-3\omega;\omega,\omega,\omega)$ was determined in the isotropic liquid phase by the wedge Maker fringe method. Thus, the first Stokes line at 1.907 μm from a hydrogen Raman cell, pumped by a pulsed Nd:YAG Q-switched laser (20 nsec) served as the fundamental beam which was divided into sample and reference computer controlled arms. From comparing the sample $I_L^{3\omega}$ and reference glass $I_G^{3\omega}$ third harmonic intensities, the liquid macroscopic $\chi_L^{(3)}$ was determined relative to glass with $\chi_G^{(3)} = 1.17 \times 10^{-14}$ esu according to the expression

$$\frac{I^{3\omega}}{I_G^{3\omega}} = \left(\frac{\chi_L^{(3)} \ell_c}{\chi_G^{(3)} \ell_c^G} \right)^2 \left(\frac{I^{\omega}}{I_G^{\omega}} \right)^3$$

where l_c and l_c^G [$l_c = \lambda/6(n^{3\omega}-n^{\omega})$] are the coherence lengths of the sample and glass, respectively. At λ=1.907 mm (0.65 eV), $\chi^{(3)}$ and l_c for TBTZ are 0.19×10^{-12} esu and 5.2 μm, respectively. Through refractive index measurements of TBTZ, we obtain $n_\omega = 1.62$ and $n_{3\omega} = 1.68$.

For an isotropic liquid, $\chi_L^{(3)}$ is related to the effective microscopic third order susceptibility $\gamma_L(-3\omega;\omega,\omega,\omega)$ by

$$\chi_L^{(3)} = N \left(\frac{2 + n_\omega^2}{3} \right)^3 \left(\frac{2 + n_{3\omega}^2}{3} \right) \gamma_L$$

where N is the number density, γ_L the orientational average of the microscopic susceptibility $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)^3$, and the refractive index terms are local field factors. Corrections are made for reflections at the boundaries and for the third order contributions of the surrouncing atmosphere.

The frequency dependent microscopic $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ shown in Figure 2 was theoretically determined by SCF-MO-SDCI calculations including singly and doubly excited configurations to account for electron correlations. At λ=1.907μm (0.65 eV), the calculated γ_L value 11 x 10^{-36} esu agrees well with the experimental value of 13 x10^{-36}esu. The major finding is that the microscopic origin of $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is determined by virtual excitations to highly correlated two photon ^1A_g π-electron states through the first principal one photon ^1B_u excited state. Important features of the highly correlated virtual processes are compactly described by contour diagrams of the transition density matrix $\rho_{nn'}$. Figure 3a shows $\rho_{nn'}$ for the ^1A_g ground and ^1B_u excited states, and Figure 3b $\rho_{nn'}$ for the ^1B_u and two photon ^1A_g excited states. We demonstrate the necessity of including doubly excited configurations in third order calculations as well as the important roles of symmetry and two photon states in third order processes.

Figure Captions

Figure 1. Rigid rod structure of TBOZ(trans-benzobisoxazole). (For TBTZ (trans-benzobisthiazole) replace O with S.)

Figure 2. Calculated frequency dependent $\gamma_L(-3\omega;\omega,\omega,\omega)$. Results essentially the same for TBOZ and TBTZ. (Insert : Experimental and calculated optical absorption spectra of TBOZ. Solid line: theoretical; dotted line: experimental gas phase; dashed line: experimental solution phase in dioxane.)

Figure 3. Contour diagram of transition density matrix $\rho_{nn'}$ for (a) ^1A_g ground and ^1B_u excited states and (b) ^1B_u one photon and ^1A_g two photon excited states of TBOZ.

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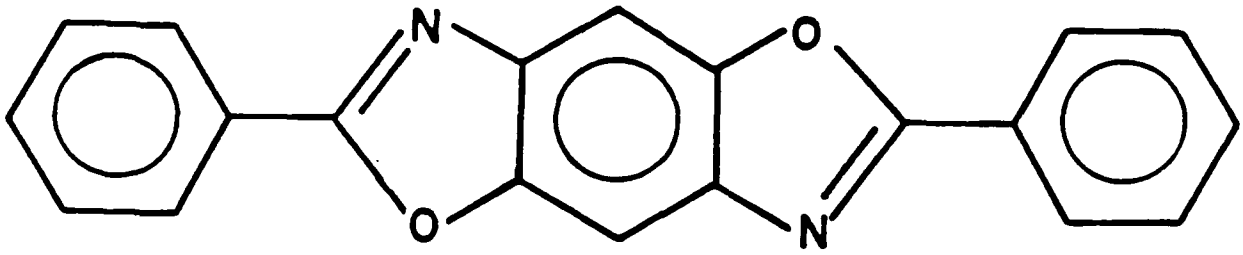
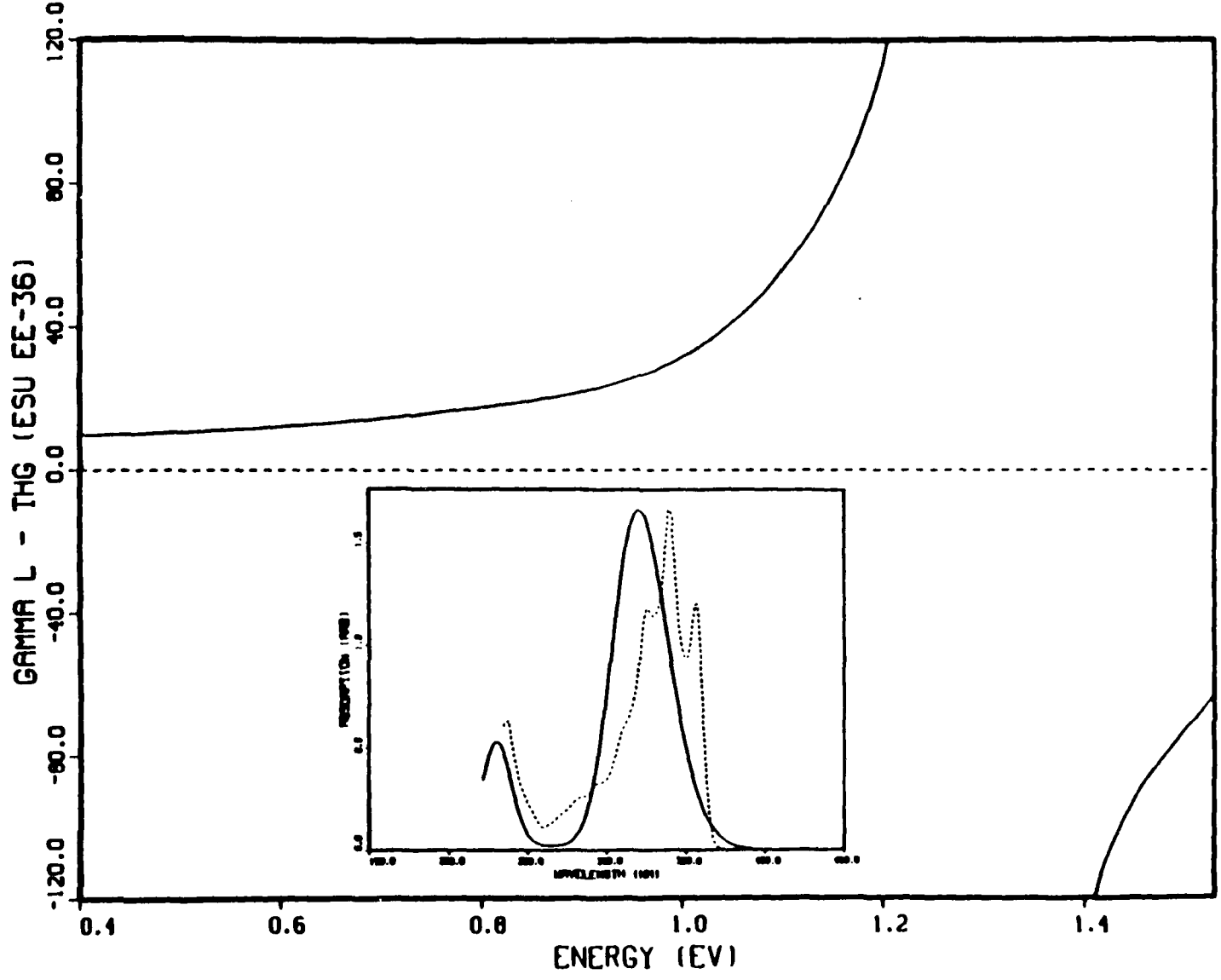
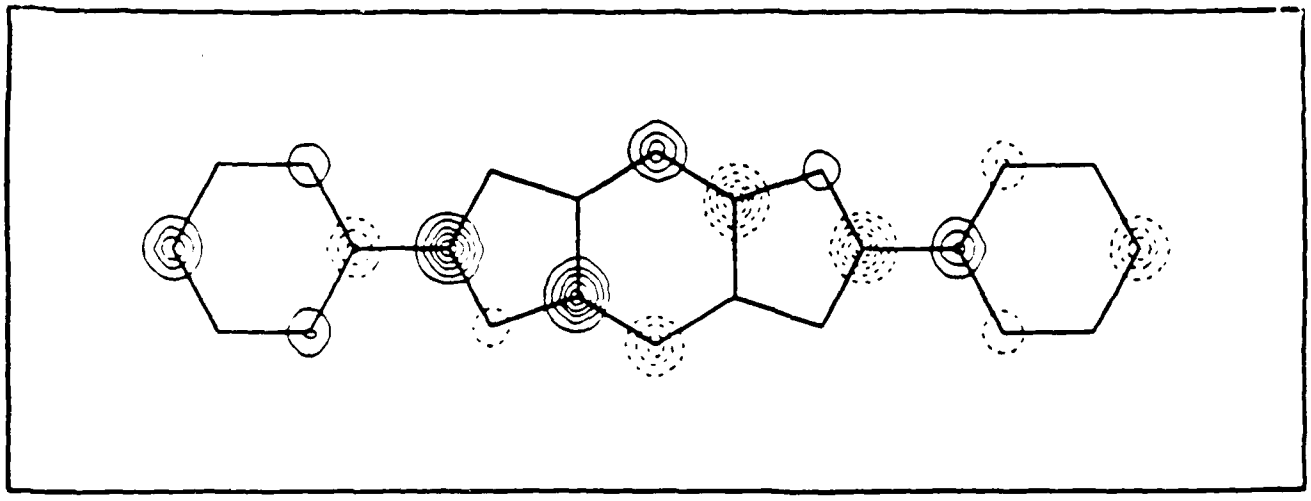
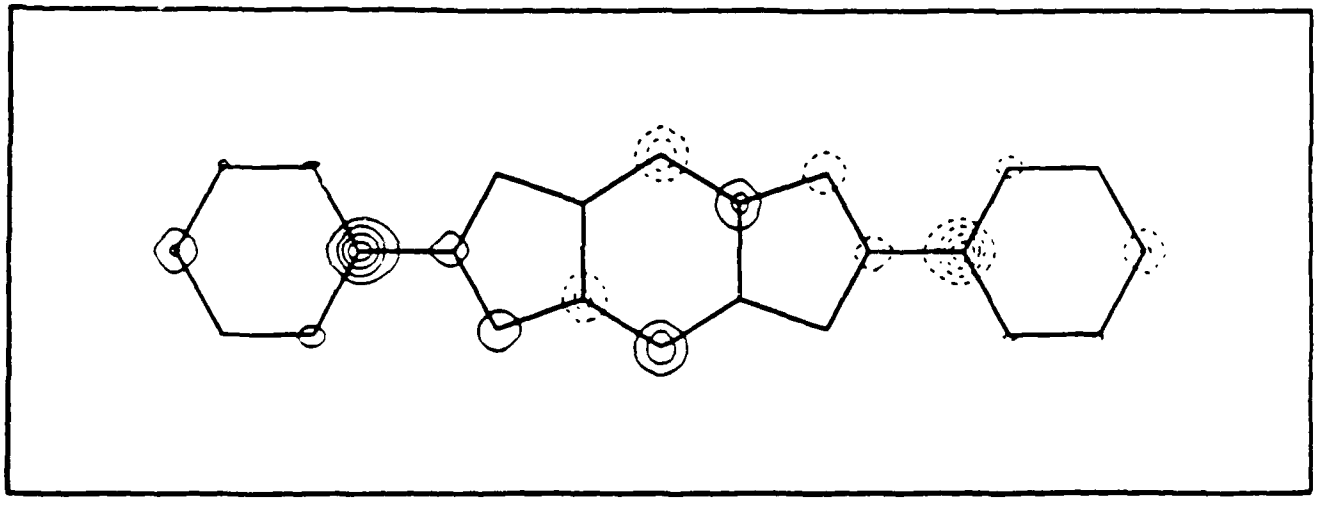


TBOZ


GAMMA L - THG (ESU EE-36)
120.0
80.0
40.0
0.0
-40.0
-80.0
-120.0
0.4
0.6
0.8
1.0
1.2
1.4
ENERGY (EV)



(a)



(b)

APPENDIX D

"RIGID AROMATIC HETEROCYCLIC POLYMERS
FOR NONLINEAR OPTICS"

Proceedings of SPIE-The International Society for Optical Engineering,
Vol. 682 "Molecular and Polymeric Optoelectronic Materials:
Fundamentals and Applications," Ed. Garo Khanarian, 1986

Invited Paper

Rigid aromatic heterocyclic polymers for nonlinear optics

James F. Wolfe

Polymer Sciences Department
SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025

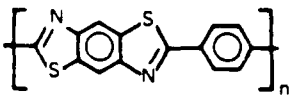
Introduction

The use of organic polymers for nonlinear optical (NLO) processes is gaining increased attention because of the ability to engineer molecular structures that have high laser damage thresholds, high values of both the first and second hyperpolarizabilities, and inherently fast response times. This general class of materials also provides synthesis and processing options that are not feasible with inorganic crystals, such as structural optimization through modification, fiber spinning, film casting and thermoplastic processes.

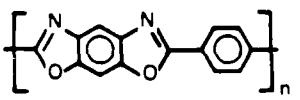
This paper provides the synthesis method for a class of polymers commonly referred to as the PBZ polymers. One of these polymers, namely poly(p-phenylene-2,6-benzobisthiazole) (PBT) has been shown to have a high value of the macroscopic third order optical nonlinear susceptibility, $\chi^{(3)}$.[1] Development of the synthesis of these π-electron conjugated systems combined with their evaluation for nonlinear optical responses may be viewed to be the preliminary step in the engineering of optimized materials for use in optical signal processing devices of the future. By describing the process of preparing rigid rod and semi-rigid benzothiazole and benzoxazole polymers in polyphosphoric acid (PPA) at the appropriate concentration to achieve the advantages of highly ordered solution morphologies, we establish the foundation for the preparation of materials with optimized figures of merit for NLO applications.

Background

Ten years ago the Air Force Materials Laboratory and the Air Force Office of Scientific Research identified an area of research called the Ordered Polymers Program aimed at the synthesis and processing of particularly rigid polymers for use in aerospace vehicles where the properties of high strength, high modulus, and environmental stability were key goals.[2] Guided by earlier work on the rigid ladder polymer BBL,[3] initial research focused on "rigid rod" aromatic heterocyclic structures, namely PBT[4] and poly(p-phenylene-2,6-benzobisoxazole) (PBO).[5] The structure-property relationships that originally led to the molecular design of PBT and PBO were (1) the rigid rod structure to impart liquid crystalline orderability and (2) a wholly aromatic structure to impart high modulus and thermal and thermooxidative stability. The fully conjugated nature of these linear π-electron systems now makes them good candidates for NLO applications.



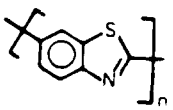
PBT



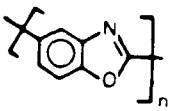
PBO

The first preparations of both of these polymers were conducted at polymer concentrations of 3 wt%. The polymers remained in the isotropic phase throughout the polymerization but gave samples of sufficient molecular weight that liquid crystalline solutions could be obtained by redissolution in methanesulfonic acid. The mechanical properties of fibers obtained by processing these ordered solutions were significantly higher for PBT[6] than for PBO[5b] and the better performance was ascribed to the higher molecular weight of PBT ($[\eta]$ = 18 dL/g for PBT vs. $[\eta]$ = 3.8 dL/g for PBO). The chemistry of the benzobisthiazole formation was believed at the time to lead inherently to much higher molecular weight polymer than could be achieved with the benzobisoxazole system and therefore research and development began to focus on the PBT system.

As we investigated the process of preparing PBT in polyphosphoric acid (PPA) and progressed to larger reaction scales, polymerization at higher solids concentration became a necessity. Polymerizing in the range of 5-10 wt% we observed that PBT formed the liquid crystalline phase during polymerization and higher molecular weights were achieved. On another project at the same time we were investigating the polymerization of poly(2,6-benzothiazole) (ABPBT) as a potential matrix resin for PBT and were polymerizing within this same concentration range of 5-10 wt%. These polymerizations remained isotropic (as we fully expected) and intrinsic viscosities no greater than 5 dL/g were obtained. When concentrations greater than 10 wt% were attempted using conventional PPAs (i.e., PPAs with



ABPBT



ABPBO

P_2O_5 contents in the range of 83.3 - 84.9%), low molecular weight polymers were obtained. It became apparent that at these higher concentrations the increased amount of water of condensation (relative to the PPA) was causing hydrolysis of the PPA to give compositions that were less effective as polymerization media in the late stages of the polycondensation. A new process, called the adjustable P_2O_5 content polymerization process, was developed whereby the P_2O_5 content of the PPA at the beginning of the polymerization was increased by adding a calculated amount of solid P_2O_5 such that an effective PPA composition (P_2O_5 content > 82%) resulted at the end of the polymerization.[7]

Results and Discussion

The major consequences of the development of the adjustable P_2O_5 content polymerization process are summarized in Table 1. Polymerization of the rigid rods PBT and PBO at concentrations greater than 10 wt% provided not only economic advantage but allowed the preparation of higher molecular weight polymers in a liquid crystalline solution that could be processed directly into highly ordered fiber and film. The ability to polymerize at the higher concentrations allowed the discovery that semi-rigid polymers, such as ABPBT and poly(2,5-benzoxazole) (ABPBO), could form nematic phases. Polymerization in the nematic phase gave high molecular weight polymers of this type for the first time.

The adjustable P_2O_5 content polymerization process can be graphically represented by plotting the P_2O_5 content versus the polymerization time line as shown in Figure 1. All PBZ polymerizations are best conducted by using a hydrochloride salt of the first monomer with the hydrogen chloride protecting group being replaced by PPA in the initial phase of the process, thereby activating the monomer toward condensation with the carboxyl group. The P_2O_5 content is lowered to reduce the bulk viscosity during this dehydrochlorination phase to aid in the removal of the gaseous HCl. Solid P_2O_5 is then added according to the equation given in the experimental section to raise the P_2O_5 content to the proper level. Polymerization is then conducted at temperatures between 165 and 185°C.

Plotting the intrinsic viscosity of samples isolated from the reaction mixture versus polymerization time for a PBT polymerization conducted at a concentration of 14.5 wt% and with a final P_2O_5 content of 83.24% shows a very rapid polymerization rate. See Figure 2. Intrinsic viscosities of greater than 20 dL/g can be achieved in less than two hours by this method. In contrast, Figure 3 shows a polymerization conducted at a relatively high polymer concentration but with a final P_2O_5 content that is insufficient to maintain a suitable polymerization rate and the desired level of molecular weight is never achieved. Figure 4 shows that a rapid polymerization can be maintained until the desired molecular weight is achieved when the polymerization is conducted with the use of an endcapping agent. This endcapping method provides a polymer solution that is stable with respect to molecular weight and thus can be processed at high temperature without rheological changes.

Table 1. Adjustable P_2O_5 Content Polymerization Process[7]

	Polym'n[a] Conc., wt %	Max $[\eta]$[b] dL/g
PBT	17	36 – 48
PBT-PBO	15	26
ABPBT	20	17
PBO	14	26
ABPBO	17	18
LC copolymers		
LC block copolymers		

[a]Concentration of polymer during polymerization. [b]Highest intrinsic viscosity (in MSA at 30°C) achieved at given polymerization concentration.

Three basic observations resulted from this work that are applicable to the PPA synthesis of a broad family of rigid and semi-rigid polymers:

- Polymerizations conducted at concentrations such that the liquid crystalline phase forms at relatively low conversion proceed to form higher molecular weight polymer than those conducted in the isotropic phase (See Figure 5).

- Certain semi-rigid polymers, such as ABPBT and ABPBO, form the liquid crystalline phase at much higher concentrations than the rigid rod polymers. The concentration required varies and depends on the degree of flexibility imparted to the backbone by the angle of catenation of the repeat unit.

- The liquid crystalline solutions of ABPBT and ABPBO obtain only if they are prepared from monomer at high concentration. Redissolution of an isolated, high molecular weight, semi-rigid polymer proceeds through a dilute phase in which conformations other than the extended chain planar zig-zag become entangled and are prevented from rotating into the proper conformation for the ordered phase.

Experimental procedures

Monomer synthesis

The syntheses of the required monomers for the PBZ family of polymers are provided in reference 7.

Polymer synthesis

The first stage of the polymerization is the dehydrochlorination of the amino-thiol or amino-hydroxy monomer in an "initial PPA" having a P_2O_5 content of P_1. The weight of the initial PPA used is given by A in Equation 1, where Ŷ is the theoretical polymer yield in

$$A = \frac{\hat{Y}\{[1-P_f][(1/C)-1] - n(18.02)/M\}}{(1-P_1)} \quad (1)$$

grams, P_f is the desired P_2O_5 content at the end of polymerization, C is the polymer weight fraction in the final mixture, n is the moles of water formed in the condensation per mole of repeat unit, and M is the molar weight of the repeat unit. Dehydrochlorination is conducted at < 100°C under reduced pressure, the carboxylic acid monomer is added (if necessary) and then B grams of P_2O_5 is added according to Equation 2. The polymerization is then conducted

$$B = \hat{Y}\{(1/C) - 1 - n(18.02)/M\} - A \quad (2)$$

at 165 - 185°C for 2 - 6 h. The appropriate choices of P_1, C, and P_f for specific polymers are presented in Ref. 7. In general, P_1 is chosen to give a low bulk viscosity that aids in evolution of the HCl, C is chosen to be above the critical concentration for the formation of the liquid crystalline phase and below the solubility limit of monomer and polymer. The operable range of concentrations for PBT is between 5 and 18 wt% (i.e., C = 0.05-0.18). The solubility of PBO is somewhat lower than PBT giving optimal concentrations of 5-14 wt% (C = 0.05-0.14). The full advantage of polymerizing in the liquid crystalline phase is not realized for ABPBT until a concentration of 13 wt% is used with the solubility limit at approximately 21 wt%. ABPBO forms the liquid crystalline phase at a relatively early stage in the polymerization at a slightly higher concentration than is observed for ABPBT and has a lower solubility. The operable range for ABPBO is thus C = 0.145-0.18. The final P_2O_5 content, P_f, is chosen to be between 0.82 and 0.84.

PBZ properties

PBZ polymers are among the most thermally and thermooxidatively stable polymers known. As shown by isothermal aging in circulating air at 371°C, fibers of ABPBO, for example, lose approximately 10% of their weight after 200 h. (See Figure 6) PBT yarns retain high percentages of both tensile strength and modulus when tested at temperatures of 300°C.[6]

Dry-jet wet spinning of the polymerization mixture (as produced by the above process) has produced PBT fibers with as-spun modulus and tenacity as high as 2050 gpd (42 Msi) and 20 gpd (400 Ksi), respectively.[8] Through appropriate heat treatment of the PBT fiber, these values were increased to 2600 gpd (53 Msi) and 30 gpd (615 Ksi), respectively, with an elongation of 1.1 percent. Efforts are continuing at both Du Pont and Celanese, under Air Force support to optimize and scale up the fiber spinning process.

At Celanese Research Company, PBT solutions have been processed into uniaxially oriented ribbons (1.0 in x 0.5 mil) with as-spun properties of 650 gpd (13 Msi) modulus, 13 gpd

(250 Ksi) tenacity, and 3.6 percent elongation.[9] Heat treatment of the ribbons increased the modulus and tenacity values to 1800 gpd (37 Msi) and 25 gpd (512 Ksi), respectively, and decreased the elongation to one percent.

Acknowledgements

The author gratefully acknowledges the support of the Air Force Office of Scientific Research (AFOSR) and the Polymer Branch of the Air Force Materials Laboratory (AFWAL/MLBP).

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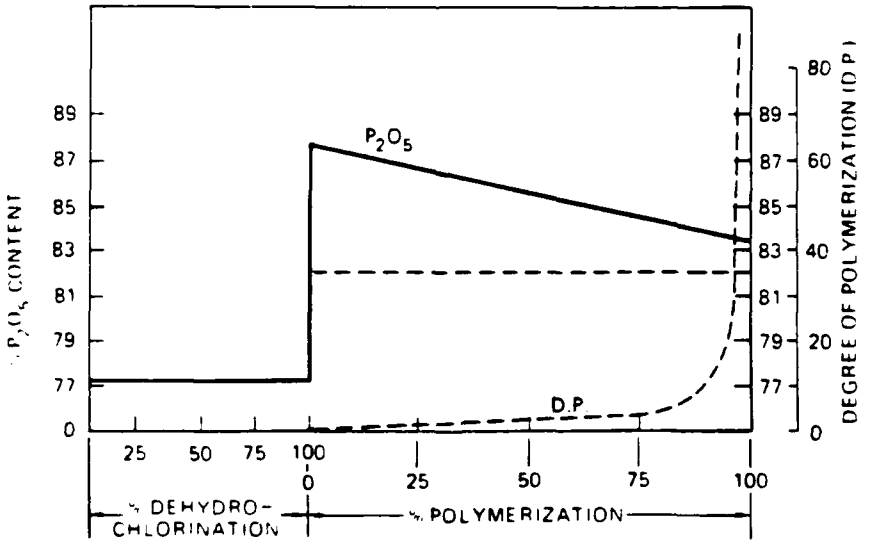

Figure 1. P_2O_5 content profile of a typical PBZ polymerization (14.5 wt% PBT) showing the calculated intermediate P_2O_5 content required to achieve an effective P_2O_5 content of 83.5% at the end of the polymerization.

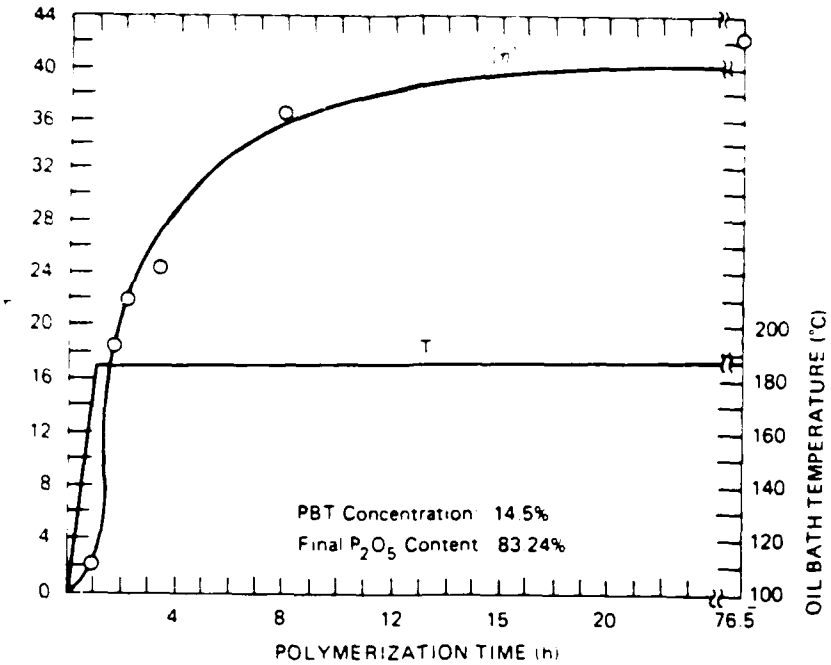

Figure 2. Intrinsic viscosity and polymerization temperature versus polymerization time for a PBT polymerization with a high PBT concentration and a high final P_2O_5 content.

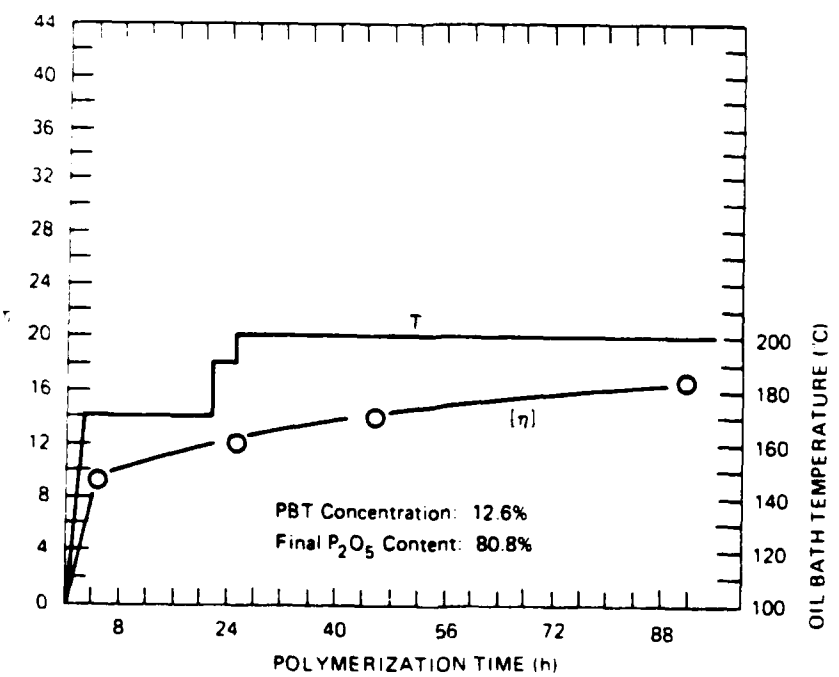

Figure 3. Intrinsic viscosity and polymerization temperature versus polymerization time for a PBT polymerization with a high PBT concentration and a low final P_2O_5 content.

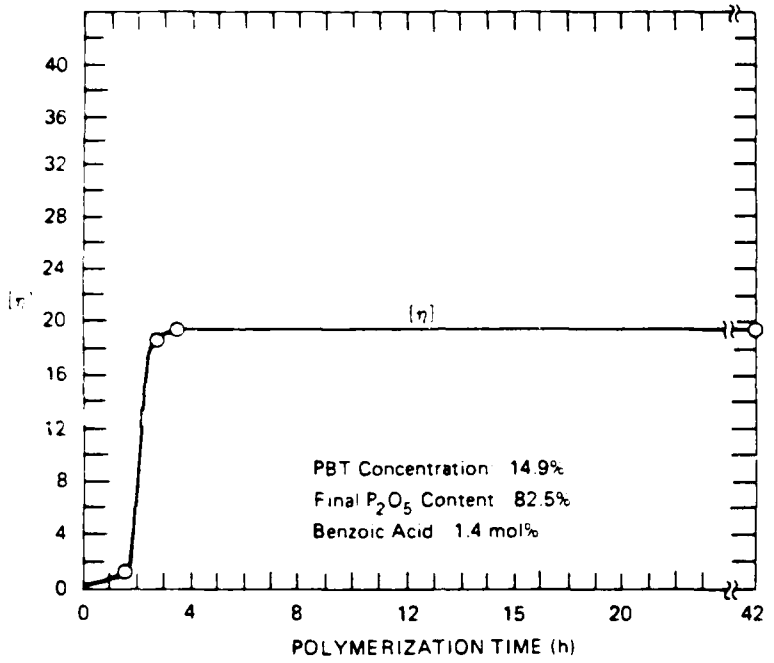

Figure 4. Intrinsic viscosity versus polymerization time for a PBT polymerization employing 1.4 mol% of benzoic acid as an endcapper with a high PBT concentration and sufficiently high final P_2O_5 content.

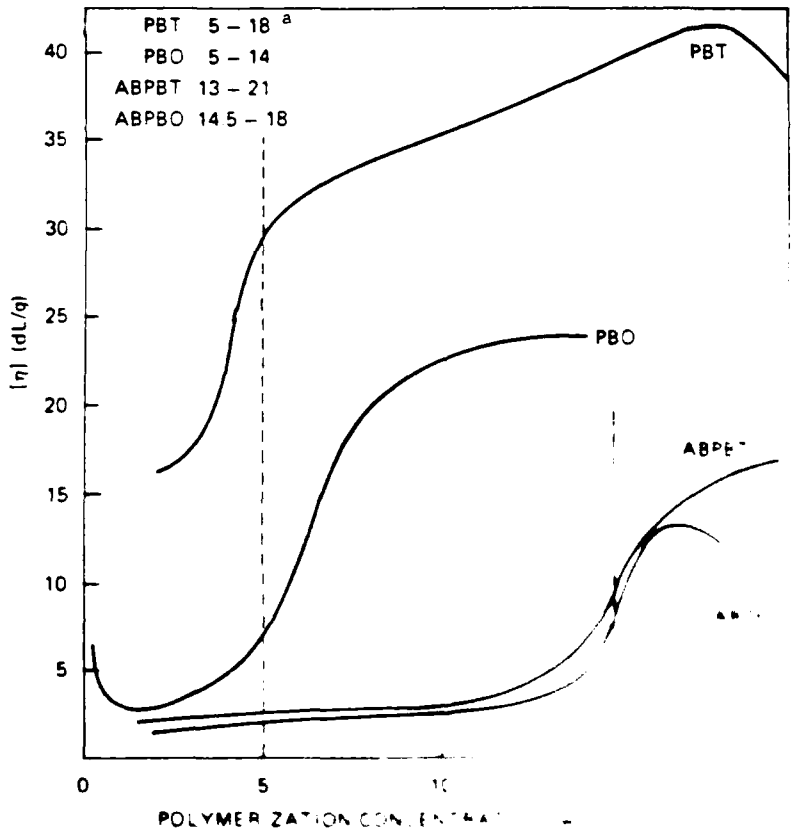

Figure 5. Maximum achievable intrinsic viscosity versus polymerization concentration for three [illegible]

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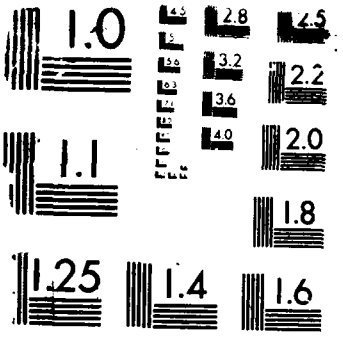

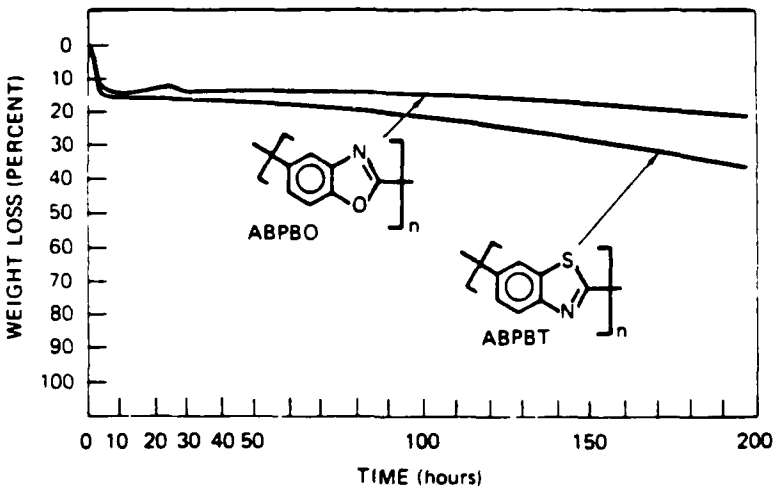

Figure 6. Isothermal aging of ABPBO and ABPBT in circulating air at 371°C.

APPENDIX E

"SYNTHESIS AND SOLUTION PROPERTIES OF
SOME EXTENDED CHAIN POLY(BENZAZOLES)"

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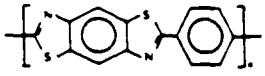
SYNTHESIS AND SOLUTION PROPERTIES OF SOME EXTENDED CHAIN POLY(BENZAZOLES)

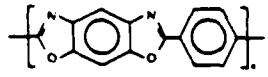
A. W. Chow, P. E. Penwell, S. P. Bitler, and J. F. Wolfe
SRI International, 333 Ravenswood Ave., Menlo Park, CA 94025

INTRODUCTION

Our studies of aromatic heterocyclic polymers of the poly(benzazole) family are motivated by the need for lightweight, high strength, high modulus, environmentally resistant materials for use in structural applications. Within the Air Force's Ordered Polymers Research Program, our original approach focused on the rigid rod polymer structures PBT[1] and PBO[2] that formed liquid crystalline phases during polymerization at concentrations above 5 wt%.

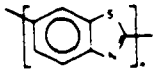


PBT

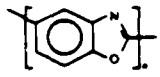


PBO

In developing the synthesis methods for the preparation of PBT in poly(phosphoric acid) (PPA), we discovered that polymerization was possible at polymer concentrations as high as 21 wt% if the P_2O_5 content of the PPA was increased to account for the greater relative amount of water of condensation.[3] The ability to polymerize at concentrations greater than 14 wt% allowed the discovery that less rigid polymers such as poly(2,5-benzothiazole) (ABPBT) and poly(2,6-benzoxazole) (ABPBO) also formed the liquid crystalline phase during polymerizations.



ABPBT



ABPBO

These molecules are characterized by catenation angles (angle between exocyclic bonds of rigid backbone units) of 162° for ABPBT and 150° for ABPBO. Because of the unrestricted rotation between repeat units, the molecule can assume either an extended chain conformation or a coil-like conformation. In dilute solutions, these polymers are likely to assume a random distribution of cis- and trans-conformations because neither conformation is expected to be statistically favored.

Using low angle light scattering and viscometry, we report our preliminary findings in our study of the dilute solution properties of ABPBT and ABPBO.

THEORETICAL CONSIDERATIONS

Light Scattering from Semirigid Polymers

Light scattering from an anisotropic element of a polymer chain involves the intrinsic anisotropy factor δ_o defined as[4]

$$\delta_o^2 = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2}{2(\alpha_1 + \alpha_2 + \alpha_3)^2} \qquad (1)$$

where α_1, α_2, and α_3 are the principal polarizabilities of the scattering element. The overall anisotropy of the chain, δ, is dependent on the chain conformation in addition to δ_o. δ can be defined as an average of δ_o for each chain segment over conformation space. For a wormlike chain with contour length L and persistence length ρ, δ derived from theory[5] is

$$\delta^2 = \delta_o^2 \left(\frac{2}{3Z}\right)\{1 - \exp(-3Z)\} \qquad (2)$$

where $Z = L/\rho$.

For low angle light scattering (LALS), the equations describing the Rayleigh ratios R_{VV} and R_{HV} for the vertical and horizontal components of light scattered in the transverse plane with vertically polarized incident light can be written as[6]

$$\lim_{\theta \to 0} [R_V/KMc] = 1 + \frac{4}{5}\delta^2 - 2A_2Mc + O(c^2) \qquad (3)$$

$$\lim_{\theta \to 0} [R_H/KMc] = \frac{3}{5}\delta^2 + O(c^2) \qquad (4)$$

A_2 is the second virial coefficient, M is the molecular weight, c is the solution concentration, and K is an optical constant related to the intrinsic optical properties of the polymer-solvent system.

Intrinsic Viscosity of Stiff Chains

A wormlike cylinder model has been proposed by Yamakawa and Fujii[7] to evaluate the intrinsic viscosity of stiff chains. The model requires three molecular parameters--contour length L, persistence length ρ, and molecular diameter d--to evaluate the intrinsic viscosity $[\eta]$

$$[\eta] = \Phi(L/\rho)^{3/2}\rho^3/M \qquad (5)$$

Φ is a function of (L/ρ) and (d/ρ), and M is the molecular weight.

Evaluation of Persistence Length and Molecular Diameter

As discussed above, ρ is one parameter required for theory calculations of LALS and viscometry results. It is therefore desirable to obtain an independent estimate of ρ.

Flory and coworkers have proposed a virtual bond model[8] to evaluate chain flexibility of polymers having catenation angles less than 180°. If γ is the acute angle between consecutive ring axes, ζ is the angle between the virtual bond and the exocyclic bond, and l is the virtual bond length (see Figure 1), then ρ can be estimated as

$$\rho = l[(u + \beta v)/(1 - \alpha)] \qquad (6)$$

where $\alpha = \cos\gamma$, $\beta = \sin\gamma$, $u = \cos\zeta$, and $v = \sin\zeta$.

We estimated ρ for ABPBT and ABPBO based on their molecular geometry such as bond lengths and bond angles taken from x-ray crystallographic results on oriented fibers.[9] For ABPBT, $\gamma = 18°$, $\zeta = 16.2°$, l = 6.08 Å, and the persistence length is calculated to be 130 Å. For ABPBO, $\gamma = 30°$, $\zeta = 17°$, l = 5.90 Å, and ρ is 50Å. ABPBO has a lower value of ρ because of its higher value of γ.

In addition to ρ, d is another parameter required to calculate $[\eta]$ from the Yamakawa and Fujii model. We estimated d for the ABPBZ polymers using the orthogonal distance from the extended chain axis to the atom farthest from the axis (see Figure 1). This estimate yields d = 5.5 Å for ABPBT and 7.5 Å for ABPBO.

EXPERIMENTAL

All polymer samples were prepared according to Ref. 3, precipitated in water, washed in a Soxhlet extractor to remove residual PPA, and dried under reduced pressure for 24 h to ensure complete removal of moisture. The dried samples were then stored in a desiccator until used. Methanesulfonic acid (MSA) was distilled and stored under dry nitrogen. The prepared solutions were used within three days.

Light scattering measurements were made using a Chromatix LALS

photometer equipped with a polarizing filter to measure the vertical and horizontal components of the scattered light. In addition, a band pass filter was used to remove fluorescence. The weight average molecular weight M_w, overall anisotropy δ^2, and second virial coefficient A_2 can be calculated from Eq. (3) and (4).

Intrinsic viscosity measurements were determined in MSA at 30°C using a Ubbelohde viscometer. The following equations were used to calculate [η].

$$\ln \eta_r/c = [\eta] - k'[\eta]^2 c \qquad (7)$$

$$\eta_{sp}/c = [\eta] + k''[\eta]^2 c \qquad (8)$$

η_r is the flow time ratio between the solution and the solvent, and $\eta_{sp} = \eta_r - 1$. Extrapolation of $\ln \eta_r/c$ and η_{sp}/c to infinite dilution should result in the same intercept which is [η].

RESULTS AND DISCUSSIONS

An empirical equation called the Mark-Houwink relationship relates intrinsic viscosity to molecular weight by

$$[\eta] = K M_w^a \qquad (9)$$

where K and a are empirically determined constants.

Figure 2 is a bi-logarithmic plot of [η] (determined by viscometry) versus M_w (determined by LALS). The slope of the curve is the Mark-Houwink exponent a. For ABPBZ polymers, a is found to be about unity experimentally. This value is between a = 1.8 for rodlike polymers (such as PBT) and a = 0.5 for random coil polymers in (such as polyethylene) theta solvent, indicating a semi-flexible structure for this class of polymers.

The solid line in Figure 2 is the wormlike cylinder model prediction of [η] using d = 5.5Å and ρ = 130Å. These values of d and ρ were obtained from geometric analysis of the ABPBT molecular structure as discussed in the theory section. Model comparison with the ABPBT data (circles) is surprisingly good. In addition, both the theory and the experimental results show a gradual increase in slope (hence the value of exponent a) with decreasing M_w for semirigid chains.

Similar [η] calculations, denoted by the broken line, were obtained for ABPBO based on the model estimate of d = 7.5 Å and ρ = 50Å. In this case, the model fits poorly with the ABPBO results (diamonds). This discrepancy can be greatly reduced by increasing ρ from 50 Å to 90Å as indicated by the dash-dot line.

Figure 3 plots the LALS results of δ^2/δ_o^2 versus L/ρ. The solid line is the model calculations using Eq. (2). The anisotropy factor δ^2 has been normalized by δ_o^2, which was estimated after model comparisons with experimental data were made. The measured molecular weight was first reduced to the contour length L, and then normalized by the persistence lengths with ρ = 130Å for ABPBT and ρ = 90Å for ABPBO. The comparison of the experimental data to the model prediction is satisfactory. The scatter in the data points is due to the difficulty in obtaining good measurements of R_{HV}.

The second virial coefficient, A_2, was found to be about 0.01 to 0.02 cm^3 mole/g^2 for both ABPBZ polymers. Compared to many hydrocarbon polymers in organic solvents, A_2 for these heterocyclic aromatic polymers is one to two orders of magnitude higher.

ACKNOWLEDGMENT

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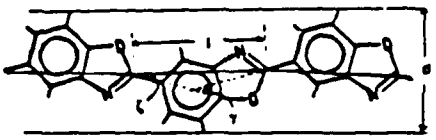

FIGURE 1

GEOMETRIC PARAMETERS NEEDED FOR THE THEORETICAL EVALUATION OF ρ AND d

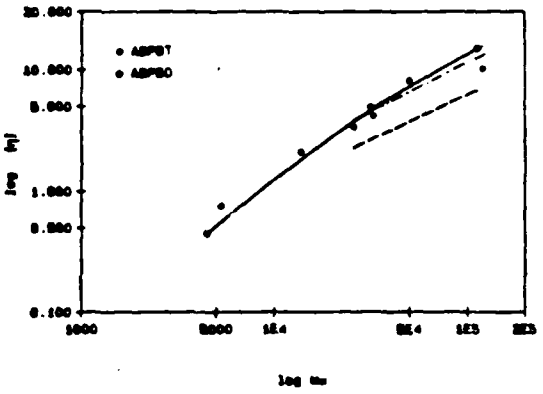

FIGURE 2

MARK-HOUWINK RELATIONSHIP FOR ABPBZ POLYMERS

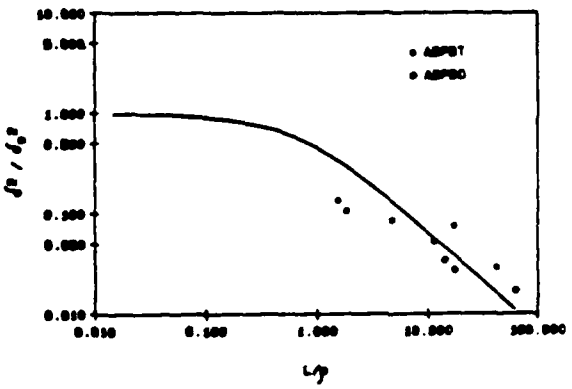

FIGURE 3

ANISOTROPY FACTOR DETERMINED BY LALS FOR ABPBZ POLYMERS

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